(REV 08/01) U S DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 36 U.S.C. 371

ATTORNEY'S DOCKET NUMBER	U.S. APPLICATION NO. (If known, see 37 CFR 1.5)
BDL-360XX	09/936596

INTERNATIONAL APPLICATION NO.	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED
PCT/FR00/00644	March 16, 2000	March 16, 1999

TITLE OF INVENTION
METHOD AND DEVICES FOR STERILIZATION BY PLASMA

APPLICANT(S) FOR DO/EO/US
Séverine Bousquet, Philippe Destrez, Marie-Pierre Jaffrezic, François Perruchot

Applicant herewith submits to the United states Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
   a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
   b. ☒ has been transmitted by the International Bureau.
   c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
   a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
   b. ☐ have been transmitted by the International Bureau.
   c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
   d. ☒ have not been made and will not be made.
8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 16. below concern document(s) or information included:

11. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☒ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A FIRST preliminary amendment.
    ☐ A SECOND or SUBSEQUENT preliminary amendment.
14. ☐ A substitute specification.
15. ☐ A change of power of attorney and/or address letter.
16. ☐ Other items or information:

8 sheets of formal drawings
Verification of Translation of PCT/FR00/00644

Express Mail Number
EL 751779258 US

U.S. APPLICATION NO. (If known, see 37 CFR 1.5)	INTERNATIONAL APPLICATION NO	ATTORNEY'S DOCKET NUMBER
09/936596	PCT/FR00/00644	BDL-360XX

17. ☒ The following fees are submitted:

	CALCULATIONS PTO USE ONLY
BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)):	
Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO **$1,000.00**	
International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO **$860.00**	
International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO **$710.00**	
International preliminary examination fee paid to USPTO (37 CFR 1.482) but all claims did not satisfy provisions of PCT Article 33(1)-(4) **$690.00**	
International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4) **$100.00**	
ENTER APPROPRIATE BASIC FEE AMOUNT =	$860.00
Surcharge of **$130.00** for furnishing the oath or declaration later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492(e)).	$ -

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	
Total claims	57 - 20 =	37	X **$18.00**	$666.00
Independent claims	2 - 3 =	0	X **$80.00**	$ -
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+**$270.00**	$ -

TOTAL OF ABOVE CALCULATIONS =	$1,526.00
☒ Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2.	$763.00
SUBTOTAL =	$763.00
Processing fee of **$130.00** for furnishing the English translation later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492(f)).	$ -
TOTAL NATIONAL FEE =	**$763.00**
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). **$40.00** per property	$40.00
TOTAL FEES ENCLOSED =	$803.00
Amount to be refunded:	$
charged:	$

a. ☒ A check in the amount of $763.00 to cover the above fees is enclosed. A check in the amount of $40.00 is enclosed for the assignment recordation fee.

b. ☐ Please charge my Deposit Account No. _____ in the amount of $_____ to cover the above fees. A duplicate copy of this sheet is enclosed.

c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 23-0804 . A duplicate copy of this sheet is enclosed.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

Customer Number 207

SEND ALL CORRESPONDENCE TO:

Weingarten, Schurgin, Gagnebin & Hayes LLP
Ten Post Office Square
Boston, Massachusetts 02109

SIGNATURE

NAME: Charles L. Gagnebin III
REGISTRATION NUMBER: 25,467

Date: 9-14-01

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application	:	SÉVERINE BOUSQUET, ET AL.
Application No.	:	
Filed	:	Herewith
For	:	METHOD AND DEVICES FOR STERILIZATION BY PLASMA
Examiner	:	
Attorney's Docket	:	BDL-360XX

Group Art Unit:

* *

I hereby certify that this correspondence is being deposited with the United States Postal Service as first class mail in an envelope addressed to: Assistant Commissioner for Patents, Washington, D.C. 20231 on _____.

By:_____
Charles L. Gagnebin III
Registration No. 25,467
Attorney for Applicant(s)

* *

PRELIMINARY AMENDMENT

BOX PCT
Assistant Commissioner for Patents
Washington, D.C. 20231

Sir:

Kindly enter the following Preliminary Amendment in the above-identified application:

In the Title:

Please amend the title to read as follows:

METHOD AND DEVICES FOR STERILIZATION BY PLASMA

Express Mail Number
EL 751779258 US

WEINGARTEN, SCHURGIN,
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In the Claims:

Please amend the Claims to read as follows (a copy of the amended claims showing the additions and deletions appears at the end for the Examiner's convenience):

1. Process for the plasma sterilization of at least one object, in which:

a) the object or objects to be treated are placed in a treatment chamber at substantially atmospheric pressure;

b) one or more non-biocidal gas mixtures, at least one of which contains moisture, are introduced into this treatment chamber;

c) a plasma, producing chemical species from one of the gas mixtures, is created by generating, by means of a high-voltage supply, an electrical discharge between a high-voltage electrode and an earth electrode, these two electrodes being placed in this treatment chamber;

d) the chemical species of the plasma are carried away out of the inter-electrode region to the surface of the object or objects to be treated; and

e) the gas residues resulting from the treatment are removed from the treatment chamber.

2. Process according to Claim 1, characterized in that the

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moisture is introduced directly around the object or objects to be treated.

3. Process according to Claim 1, characterized in that the moisture is introduced near the inter-electrode region.

4. Process according to Claim 1 characterized in that the gas mixture contains at least 10% oxygen and 10% nitrogen.

5. Process according to Claim 4, characterized in that the gas mixture consists of ambient air.

6. Process according to Claim 1, characterized in that the relative humidity around the object or objects to be treated is between 50% and 100%.

7. Process according to Claim 6, characterized in that the relative humidity around the object or objects to be treated is greater than or equal to 90%.

8. Process according to Claim 1, characterized in that step b) of introducing the gas mixture or mixtures into the treatment chamber is carried out continuously or

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intermittently.

9. Process according to Claim 8, characterized in that the flow rate of the gas mixture or mixtures entering the treatment chamber is controlled.

10. Process according to Claim 1, characterized in that step c) of creating the plasma is preceded by a step of forced circulation of the gas mixture or mixtures in the treatment chamber.

11. Process according to Claim 1, characterized in that step d) of carrying away the chemical species of the plasma to the surface to be treated is accomplished by using the electrical wind created by the discharge between the two electrodes.

12. Process according to Claim 1, characterized in that step d) of carrying away the chemical species of the plasma to the surface to be treated is accomplished by creating a forced flow in the treatment chamber.

13. Device for the plasma sterilization of at least one object,

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characterized in that it comprises:

- a first gas source containing a non-biocidal gas mixture;

- at least one treatment chamber at atmospheric pressure comprising at least one sterilization region in which the object or objects to be treated are placed, this chamber furthermore including, in at least one plasma generation region separate from the sterilization region, at least two electrodes connected to a high-voltage supply in order to create a plasma, producing chemical species by generating an electrical discharge between these electrodes in the gas mixture introduced into the plasma generation region, the chemical species of the plasma being carried away out of the plasma generation region to the surface of the object or objects to be treated and the gas residues resulting from the treatment being removed to a recovery system via an outlet port of this chamber; and

- a humidifying chamber connected downstream of a second gas source in order to maintain a defined moisture content around the object or objects to be treated.

14. Device according to Claim 13, characterized in that the first and second gas sources form a single gas source.

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15. Device according to Claim 14, characterized in that the plasma generation region is connected to this single gas source via the humidifying chamber.

16. Device according to Claim 14, characterized in that the plasma generation region is connected directly to this single gas source, the sterilization region being connected to this single gas source via the humidifying chamber.

17. Device according to Claim 13, characterized in that the sterilization region is connected to the second gas source via the humidifying chamber, the plasma generation region being connected directly to the first gas source.

18. Device according to Claim 16, characterized in that it includes a second relative humidity sensor placed upstream of the sterilization region.

19. Device according to Claim 15, characterized in that it includes a first relative humidity sensor placed upstream of the plasma generation region.

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20. Device according to Claim 13, characterized in that the gas mixture contains at least 10% oxygen and 10% nitrogen.

21. Device according to Claim 20, characterized in that the gas mixture consist of ambient air.

22. Device according to Claim 21, characterized in that the ambient air is compressed before it is humidified.

23. Device according to Claim 13, characterized in that the sterilization region has a relative humidity of between 50% and 100%, advantageously greater than or equal to 90%.

24. Device according to Claim 13, characterized in that it comprises at least one electrode with a large radius of curvature and one electrode with a small radius of curvature, one being a high-voltage electrode and the other being an earth electrode.

25. Device according to Claim 24, characterized in that the electrode with a small radius of curvature is a metal electrode which may have one of the following shapes: a wire, spikes or a wire having spikes.

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26. Device according to Claim 24, characterized in that the electrode with a large radius of curvature is a metal electrode which may have one of the following shapes: a wire, a plane, or a mesh or solid cylinder.

27. Device according to Claim 25, characterized in that one or the other of the two electrodes, or both electrodes, are covered with a dielectric coating.

28. Device according to Claim 25, characterized in that the high-voltage electrode consists of a wire and in that the earth electrode consists of a mesh cylinder surrounding this wire.

29. Device according to Claim 24, characterized in that the electrodes are mounted as an array of parallel electrodes, the high-voltage electrodes being supplied in succession or simultaneously.

30. Device according to Claim 13, characterized in that the electrodes are of limited usage.

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31. Device according to Claim 13, characterized in that the high-voltage supply is provided by a low-frequency generator delivering a DC voltage, square-wave voltage or AC voltage, or a voltage pulsed over time.

32. Device according to Claim 13, characterized in that it comprises several treatment chambers, each treatment chamber having at least one plasma generation region connected, fixedly or not, to at least one sterilization region , the plasma generation regions being connected to a common central unit containing at least the first non-biocidal gas source , the humidifying chamber , the gas residues recovery system and the high-voltage supply.

33. Device according to Claim 32, characterized in that the sterilization region of the treatment chamber has a shape specially tailored to the object or objects to be sterilized so as to limit the production of chemical species necessary for sterilization and to optimize the rate of flow and the concentration of these sterilizing species around the object.

34. Device according to Claim 33, characterized in that the treatment chamber includes a case of standard shape and

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containing the plasma generation region, the sterilization region being formed by a removable support especially tailored to the object or objects to be treated and housed in this case.

35. Device according to Claim 32, characterized in that the sterilization region includes propagation regions of small cross section making it possible to accelerate the chemical species emanating from the plasma generation region towards various parts of the object or objects to be treated.

36. Device according to Claim 32, characterized in that the plasma generation region is incorporated into the object to be treated and forms a part thereof.

37. Device according to Claim 32, characterized in that the sterilization region is separate from the plasma generation region and forms an independent chamber.

38. Device according to Claim 32, characterized in that one or more of the treatment or sterilization chambers constitute reusable autonomous packaging, in the form of a

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transportation case, allowing the sterile post-treatment state to be maintained.

39. Device according to Claim 32, characterized in that one or more of the treatment or sterilization chambers constitute disposable packaging, in the form of a flexible bag, it being possible for the sterilization region to be divided into several separate regions after the treatment, by cutting and concomitantly sealing defined parts of this bag.

40. Device according to Claim 32, characterized in that all or part of the device is placed in a Faraday cage.

41. Device according to Claim 32, characterized in that the common central control unit includes indicating and control means which are associated with each sterilization chamber in order for the sterilization of the objects that it contains to be controlled individually.

42. Device according to Claim 41, characterized in that the common central control unit includes printing means for printing a label on which will be printed, for each sterilization chamber connected to this central control unit,

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an identification number specific to each chamber together with the date of the treatment and the parameters of the stabilization cycle carried out.

43. Device according to Claim 32, characterized in that the treatment or sterilization chamber is provided with an electronic label which makes it possible, by means of a corresponding reader of the central control unit, to determine automatically the flow rate setpoint values and control current which are suitable for the object or objects to be treated and to calculate the time needed to sterilize these objects.

44. Device according to Claim 43, characterized in that the electronic label includes a velocity sensor for measuring the flow rate of the chemical species of the plasma in the chamber.

45. Device according to Claim 43, characterized in that the electronic label includes a chemical measurement sensor.

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46. Application of the device of Claim 13 to the sterilization of objects of any shape and of any nature, especially be they metallic, composite or heat-sensitive.

47. Application of the device of Claim 13 to the sterilization of the surfaces of packaging, of products or of production equipment.

48. Application of the device of Claim 13 to the decontamination of the internal surfaces of air conditioning systems.

49. Application of the device of Claim 13 to the disinfection of containment or transfer areas.

Please add the following new claims 50-57:

50. Process according to Claim 2 characterized in that the gas mixture contains at least 10% oxygen and 10% nitrogen.

51. Process according to Claim 3 characterized in that the gas mixture contains at least 10% oxygen and 10% nitrogen.

52. Device according to Claim 17, characterized in that:

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it includes a second relative humidity sensor placed upstream of the sterilization region;

the gas mixture contains at least 10% oxygen and 10% nitrogen;

the gas mixture consist of ambient air;

the ambient air is compressed before it is humidified;

the sterilization region has a relative humidity of between 50% and 100%, advantageously greater than or equal to 90%;

it comprises at least one electrode with a large radius of curvature and one electrode with a small radius of curvature, one being a high-voltage electrode and the other being an earth electrode;

one electrode with a small or large radius of curvature is a metal electrode which may have one of the following shapes: a wire, spikes or a wire having spikes, a plane, or a mesh or solid cylinder;

either one or the other of the two electrodes, or both electrodes, are covered with a dielectric coating, or the high-voltage electrode consists of a wire and in that the earth electrode consists of a mesh cylinder surrounding this wire;

the electrodes are of limited usage;

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the high-voltage supply is provided by a low-frequency generator delivering a DC voltage, square-wave voltage or AC voltage, or a voltage pulsed over time.

53. Device according to Claim 17, characterized in that it includes a first relative humidity sensor placed upstream of the plasma generation region.

54. Device according to Claim 34, characterized in that the sterilization region includes propagation regions of small cross section making it possible to accelerate the chemical species emanating from the plasma generation region towards various parts of the object or objects to be treated.

55. Device according to Claim 37, characterized in that:

one or more of the treatment or sterilization chambers constitute either reusable autonomous packaging, in the form of a transportation case, allowing the sterile post-treatment state to be maintained, or disposable packaging, in the form of a flexible bag, it being possible for the sterilization region to be divided into several separate regions after the treatment, by cutting and concomitantly sealing defined parts of this bag;

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all or part of the device is placed in a Faraday cage.

56. Application of the device of Claim 45 to the sterilization of objects of any shape and of any nature, especially be they metallic, composite or heat-sensitive, or the sterilization of the surfaces of packaging, of products or of production equipment.

57. Application of the device of Claim 45 to the decontamination of the internal surfaces of air conditioning systems or the disinfection of containment or transfer areas.

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REMARKS

This Preliminary Amendment puts the claims into proper form for examination. Please note that claims 1-4, 6-20, 23-24, 27-28, 30-35, 37-43, and 46-49 have been amended; new claims 50-57 have been added; and claims 5, 21-22, 25-26, 29, 36, and 44-45 remain unchanged. Kindly calculate the filing fee based on the amended claims.

The Examiner is encouraged to telephone the undersigned attorney to discuss any matter which would expedite allowance of the present application.

Respectfully submitted,

SÉVERINE BOUSQUET, ET AL.

By: _____
Charles L. Gagnebin III
Registration No. 25,467
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Date: 9-14-1

CLG:kmw/258380-1
Enclosure

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(Marked-up version for the convenience of the examiner)

1. Process for the plasma sterilization of at least one object, in which:

a) the object or objects ~~(50)~~ to be treated are placed in a treatment chamber ~~(10)~~ at substantially atmospheric pressure;

b) one or more non-biocidal gas mixtures, at least one of which contains moisture, are introduced into this treatment chamber;

c) a plasma, producing chemical species from one of the gas mixtures, is created by generating, by means of a high-voltage supply ~~(38)~~, an electrical discharge between a high-voltage electrode ~~(36)~~ and an earth electrode ~~(40)~~, these two electrodes being placed in this treatment chamber;

d) the chemical species of the plasma are carried away out of the inter-electrode region ~~(30)~~ to the surface of the object or objects ~~(50)~~ to be treated; and

e) the gas residues resulting from the treatment are removed from the treatment chamber.

2. Process according to Claim 1, characterized in that the moisture is introduced directly around the object

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or objects ~~(50)~~ to be treated.

3. Process according to Claim 1, characterized in that the moisture is introduced near the inter-electrode region ~~(30)~~.

4. Process according to ~~any one of~~ Claim~~s~~ 1 ~~to 3,~~ characterized in that the gas mixture contains at least 10% oxygen and 10% nitrogen.

5. Process according to Claim 4, characterized in that the gas mixture consists of ambient air.

6. Process according to ~~any one of~~ Claim~~s~~ 1 ~~to 5~~, characterized in that the relative humidity around the object or objects ~~(50)~~ to be treated is between 50% and 100%.

7. Process according to Claim 6, characterized in that the relative humidity around the object or objects ~~(50)~~ to be treated is greater than or equal to 90%.

8. Process according to Claim 1, characterized in that

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step b) of introducing the gas mixture or mixtures into the treatment chamber ~~(10)~~ is carried out continuously or intermittently.

9. Process according to Claim 8, characterized in that the flow rate of the gas mixture or mixtures entering the treatment chamber ~~(10)~~ is controlled.

10. Process according to Claim 1, characterized in that step c) of creating the plasma is preceded by a step of forced circulation of the gas mixture or mixtures in the treatment chamber ~~(10)~~.

11. Process according to Claim 1, characterized in that step d) of carrying away the chemical species of the plasma to the surface ~~(50)~~ to be treated is accomplished by using the electrical wind created by the discharge between the two electrodes ~~(36, 40)~~.

12. Process according to Claim 1, characterized in that step d) of carrying away the chemical species of the plasma to the surface ~~(50)~~ to be treated is accomplished by creating a forced flow in the

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treatment chamber ~~(10)~~.

13. Device for the plasma sterilization of at least one object, characterized in that it comprises:

- a first gas source ~~(12)~~ containing a non-biocidal gas mixture;
- at least one treatment chamber ~~(10)~~ at atmospheric pressure comprising at least one sterilization region ~~(10b, 32)~~ in which the object or objects ~~(50)~~ to be treated are placed, this chamber furthermore including, in at least one plasma generation region ~~(10a, 30)~~ separate from the sterilization region, at least two electrodes ~~(36, 40)~~ connected to a high-voltage supply ~~(38)~~ in order to create a plasma, producing chemical species by generating an electrical discharge between these electrodes in the gas mixture introduced into the plasma generation region, the chemical species of the plasma being carried away out of the plasma generation region to the surface of the object or objects to be treated and the gas residues resulting from the treatment being removed to a

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recovery system ~~(22)~~ via an outlet port ~~(44)~~ of this chamber; and

- a humidifying chamber ~~(14)~~ connected downstream of a second gas source ~~(12, 26)~~ in order to maintain a defined moisture content around the object or objects ~~(50)~~ to be treated.

14. Device according to Claim 13, characterized in that the first and second gas sources form a single gas source ~~(12)~~.

15. Device according to Claim 14, characterized in that the plasma generation region ~~(10a, 30)~~ is connected to this single gas source via the humidifying chamber ~~(14)~~.

16. Device according to Claim 14, characterized in that the plasma generation region ~~(10a, 30)~~ is connected directly to this single gas source ~~(12)~~, the sterilization region ~~(10b, 32)~~ being connected to this single gas source via the humidifying chamber ~~(14)~~.

17. Device according to Claim 13, characterized in that

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the sterilization region ~~(10b, 32)~~ is connected to the second gas source ~~(26)~~ via the humidifying chamber ~~(14)~~, the plasma generation region ~~(10a, 30)~~ being connected directly to the first gas source ~~(12)~~.

18. Device according to Claim 16 ~~or Claim 17~~, characterized in that it includes a second relative humidity sensor ~~(18b)~~ placed upstream of the sterilization region ~~(10b, 32)~~.

19. Device according to ~~any one of~~ Claim~~s~~ 15 ~~to 17~~, characterized in that it includes a first relative humidity sensor ~~(18a)~~ placed upstream of the plasma generation region ~~(10a, 30)~~.

20. Device according to ~~any one of~~ Claim~~s~~ 13 ~~to 19~~, characterized in that the gas mixture contains at least 10% oxygen and 10% nitrogen.

21. Device according to Claim 20, characterized in that the gas mixture consist of ambient air.

22. Device according to Claim 21, characterized in that

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the ambient air is compressed before it is humidified.

23. Device according to ~~any one of~~ Claim~~s~~ 13~~ to 22~~, characterized in that the sterilization region ~~(10b, 32)~~ has a relative humidity of between 50% and 100%, advantageously greater than or equal to 90%.

24. Device according to ~~any one of~~ Claim~~s~~ 13~~ to 23~~, characterized in that it comprises at least one electrode with a large radius of curvature and one electrode with a small radius of curvature, one being a high-voltage electrode ~~(36)~~ and the other being an earth electrode~~ (40)~~.

25. Device according to Claim 24, characterized in that the electrode with a small radius of curvature is a metal electrode which may have one of the following shapes: a wire, spikes or a wire having spikes.

26. Device according to Claim 24, characterized in that the electrode with a large radius of curvature is a metal electrode which may have one of the following shapes: a wire, a plane, or a mesh or solid cylinder.

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27. Device according to Claim 25 ~~or Claim 26~~, characterized in that one or the other of the two electrodes, or both electrodes, are covered with a dielectric coating.

28. Device according to Claim 25 ~~and Claim 26~~, characterized in that the high-voltage electrode consists of a wire ~~(162)~~ and in that the earth electrode consists of a mesh cylinder ~~(164)~~ surrounding this wire.

29. Device according to Claim 24, characterized in that the electrodes are mounted as an array of parallel electrodes, the high-voltage electrodes being supplied in succession or simultaneously.

30. Device according to ~~any one~~ Claim~~s~~ 13 ~~to 29~~, characterized in that the electrodes are of limited usage.

31. Device according to ~~any one~~ Claim~~s~~ 13 ~~to 30~~, characterized in that the high-voltage supply ~~(38)~~ is

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provided by a low-frequency generator delivering a DC voltage, square-wave voltage or AC voltage, or a voltage pulsed over time.

32. Device according to Claim 13, characterized in that it comprises several treatment chambers, each treatment chamber having at least one plasma generation region ~~(68; 70; 72; 132, 136, 138; 188)~~ connected, fixedly or not, to at least one sterilization region ~~(76; 78; 80; 166; 206)~~, the plasma generation regions being connected to a common central unit ~~(60)~~ containing at least the first non-biocidal gas source ~~(12)~~, the humidifying chamber ~~(14)~~, the gas residues recovery system ~~(22)~~ and the high-voltage supply ~~(38)~~.

33. Device according to Claim 32, characterized in that the sterilization region ~~(166; 206)~~ of the treatment chamber ~~(74, 130)~~ has a shape specially tailored to the object or objects ~~(134, 140; 226, 228, 230)~~ to be sterilized so as to limit the production of chemical species necessary for sterilization and to optimize the rate of flow and the concentration of these sterilizing species around the object.

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34. Device according to Claim 33, characterized in that the treatment chamber ~~(74)~~ includes a case ~~(186)~~ of standard shape and containing the plasma generation region ~~(188)~~, the sterilization region being formed by a removable support ~~(196)~~ especially tailored to the object or objects to be treated and housed in this case.

35. Device according to Claim 32 ~~or Claim 34~~, characterized in that the sterilization region includes propagation regions ~~(200)~~ of small cross section making it possible to accelerate the chemical species emanating from the plasma generation region ~~(188)~~ towards various parts of the object or objects to be treated.

36. Device according to Claim 32, characterized in that the plasma generation region is incorporated into the object to be treated and forms a part thereof.

37. Device according to Claim 32, characterized in that the sterilization region is separate from the plasma

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generation region and forms an independent chamber ~~(76, 78, 80)~~.

38. Device according to Claim 32~~ or Claim 37~~, characterized in that one or more of the treatment or sterilization chambers constitute reusable autonomous packaging, in the form of a transportation case, allowing the sterile post-treatment state to be maintained.

39. Device according to Claim 32~~ or Claim 37~~, characterized in that one or more of the treatment or sterilization chambers constitute disposable packaging, in the form of a flexible bag~~ (220)~~, it being possible for the sterilization region to be divided into several separate regions ~~(234, 236, 238)~~ after the treatment, by cutting and concomitantly sealing defined parts of this bag.

40. Device according to ~~any one of~~ Claim~~s~~ 32~~ to 39~~, characterized in that all or part of the device is placed in a Faraday cage.

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41. Device according to Claim 32, characterized in that the common central control unit ~~(60)~~ includes indicating and control means ~~(84, 86, 88, 90)~~ which are associated with each sterilization chamber in order for the sterilization of the objects that it contains to be controlled individually.

42. Device according to Claim 41, characterized in that the common central control unit ~~(60)~~ includes printing means ~~(96)~~ for printing a label ~~(94)~~ on which will be printed, for each sterilization chamber connected to this central control unit, an identification number specific to each chamber together with the date of the treatment and the parameters of the stabilization cycle carried out.

43. Device according to Claim 32, characterized in that the treatment or sterilization chamber is provided with an electronic label ~~(98a)~~ which makes it possible, by means of a corresponding reader ~~(98b)~~ of the central control unit ~~(60)~~, to determine automatically the flow rate setpoint values and control current which are suitable for the object or

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objects to be treated and to calculate the time needed to sterilize these objects.

44. Device according to Claim 43, characterized in that the electronic label includes a velocity sensor for measuring the flow rate of the chemical species of the plasma in the chamber.

45. Device according to Claim 43, characterized in that the electronic label includes a chemical measurement sensor.

46. Application of the device of Claim~~s~~ 13 ~~to 45~~ to the sterilization of objects of any shape and of any nature, especially be they metallic, composite or heat-sensitive.

47. Application of the device of Claim~~s~~ 13 ~~to 45~~ to the sterilization of the surfaces of packaging, of products or of production equipment.

48. Application of the device of Claim~~s~~ 13 ~~to 45~~ to the decontamination of the internal surfaces of air

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conditioning systems.

49. Application of the device of Claim~~s~~ 13 ~~to 45~~ to the disinfection of containment or transfer areas.

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Method and devices for sterilization by plasma

The present invention relates to the general field of the sterilization of objects and surfaces of any type and of any shape, and it relates more particularly to a plasma sterilization process and various plasma sterilization devices operating at room temperature and at atmospheric pressure.

Prior art

In the medical and agri-foodstuff fields, sterilization corresponds to a very precise level of quality. In the medical field, sterilization means destruction of all microorganisms whatever their nature. In European pharmacopoeia, an object may be regarded as being sterile if the probability that a viable microorganism is present thereon is less than or equal to 10^{-6}. The sterilization time is the time required to sterilize a "normally contaminated" object, that is to say an object containing 10^{6} bacterial spores. Thus, sterilization of an object corresponds to reducing the initial population of bacterial spores present on this object from 10^{6} spores to 10^{-6} spores, i.e. a logarithmic reduction of 12 decades.

At the present time, there are many processes allowing objects to be made and kept sterile. The article by Philip M. Schneider, published in volume 77 of the TAPPI Journal, January 1994, pages 115 to 119, gives quite an exhaustive review thereof. However, Mr. Schneider concludes his article with the observation that at the present time there is no ideal low-temperature (i.e. less than 80°C) sterilization method, that is to say a method which is very effective, quick-acting and highly penetrating, which is furthermore non-toxic and compatible with many materials, especially organic materials, and which can be simply employed with low costs.

Furthermore, the sterile state of an object must be maintained by specific packaging which has to be compatible with the sterilization method employed (i.e. permeable to the sterilizing agent) and to prevent penetration of microorganisms during the transportation and storage phases, so as to guarantee sterility of the instrument when it is next used.

Current sterilization processes are essentially based on the effect of heat or the action of biocidal gases.

Autoclaving, which relies on the action of high-temperature (at least 121°C) wet heat, is the most effective process and the least expensive to implement, but it does not allow heat-sensitive devices, which are becoming more and more common, especially in the medical field, to be sterilized.

Sterilization processes based on gases (ethylene oxide, formaldehyde or hydrogen peroxide) make use of the biocidal nature of a gas placed in a sterilization chamber and allow heat-sensitive devices to be sterilized at low temperature. However, these processes have many drawbacks: the toxicity of the gases in question, which require complex operating and control procedures; the necessity, in certain cases (for example with plastics), to carry out a phase of desorbing the toxic gas after the sterilization phase; finally, the length of the treatment, which often takes several hours. Furthermore, it should be noted that they have a limited destructive effect on certain bacterial spores (such as *Bacillus stearothermophilus* spores).

Furthermore, it is known to improve these biocidal gas sterilization processes by carrying out the treatment at low pressure (a few torr) this being conducive to diffusion of the gas or vaporization of an additional biocidal liquid throughout the entire sterilization

chamber. Likewise, these low-pressure sterilization processes may be optimized by using cycles consisting of an alternation of phases in which the pressure is increased or decreased and plasma treatment phases, as shown especially in Patent Application FR 2 759 590 deposited by Microondes Energie Systèmes SA.

It is also known to use low-pressure plasma sterilization processes which possibly allow the sterilizing effects of the biocidal gas at low pressure to be combined with the formation, in a plasma, based on a biocidal gas mixture such as H_2O_2 or a non-biocidal gas mixture (in general, simply O_2, H_2, H_2O, N_2 or a rare gas such as argon), of reactive species (with the creation of $O^\bullet$ and $OH^\bullet$ radicals and of ionized and/or excited species), the low pressure moreover limiting recombination of unstable species. In most cases, low-pressure plasmas comprise microwave or radio-frequency plasmas.

Plasma sterilization can be highly effective in the space where the plasma is created (the inter-electrode space, but, apart from the fact that the sterilization region is then very small (about a few cm in height), the characteristics of the plasma depend very strongly on the dielectric constant, on the nature and on the size of the object to be sterilized. In this case, the plasma prevents a truly homogeneous treatment over the entire surface and has a highly corrosive action on the objects to be sterilized.

It is necessary, in order to improve such a process, to dissociate the plasma generation region from the treatment region (the sterilization is then called remote plasma sterilization) so as to avoid too strong an interaction between the plasma and the object to be sterilized which, because of its nature, disturbs the field lines and degrades the surface of the object when it is placed in the inter-electrode space. It should be

noted, however, that this separation of the plasma generation region from the sterilization region is easy in a low-pressure process since the lifetimes of the radicals produced by the plasma at these pressures (approximately one torr) are long, thereby enabling them to reach the objects to be sterilized.

Despite this, the drawbacks of low-pressure plasma sterilization processes are still numerous and at the end of the day quite similar to those that exist in single sterilization using gases, namely: the high cost of the complete system comprising a vacuum-resistant chamber and a plasma generator; the complexity of the devices used to implement these processes, which limit the possible applications; the increased treatment time due to procedures related to treatment at low pressure (the time required to create a vacuum in the chamber, the volume of which is often large, and then the time to return to atmospheric pressure increase the treatment time); the impossibility of sterilizing wet objects; and the incompatibility with certain materials.

It is also known to use another process which consists in carrying out a treatment based on ozone at atmospheric pressure using a suitable device called an ozonizer. This treatment is similar to remote-plasma sterilization, the carrier gas, which is then of the dry type, containing oxygen. However, the biocidal action of ozone, which is most particularly used to disinfect water, waste and gases, is quite limited with regard to sterilization. To increase the performance, it is in general necessary to use ozone (O_3) to which another disinfecting agent has been added (for example ClO_2 so as to form ClO_3 which has a bactericidal action in the gas phase). It is also possible to humidify the ozonized gas leaving the ozonizer, or very simply to wet the objects to be sterilized, in order to facilitate the biocidal action of this ozonized gas, as

the patent US 5 120 512 (Masuda) illustrates. In general for plasma processes based on simple non-biocidal gases, separating the plasma generation region from the treatment region limits the effectiveness of the process as only species of moderate or long lifetime are still active in the region of the object. Now, since these species are less reactive than those with a short lifetime, it is necessary to increase their concentration and the treatment time. For example, it is known that almost 3 hours of treatment are needed to achieve sterilization of *Bacillus subtilis* in the presence of moisture for an ozone concentration of 1500 ppm. Such a production level requires the use of complex devices, while the high ozone concentration increases the irreversible degradation of the surfaces and materials of the objects to be sterilized. In addition, because of regulations, the production of ozone with a high concentration requires there to be, at the outlet of the system, a particularly effective ozone destroyer of the catalytic or thermal type.

Subject and definition of the invention

It is an object of the present invention therefore to provide a plasma sterilization device for implementing a process which operates at low temperature (preferably at room temperature), at a pressure equal or practically equal to atmospheric pressure, and in an open or closed environment, and which furthermore overcomes the numerous aforementioned drawbacks of the prior art.

According to the invention, what is proposed is a process for the plasma sterilization of at least one object, in which:

a) the object or objects to be treated are placed in a treatment chamber at substantially atmospheric pressure;

b) one or more non-biocidal gas mixtures, at least one of which contains moisture, are introduced into this treatment chamber;

c) a plasma, producing chemical species from one of the gas mixtures, is created by generating, by means of a high-voltage supply (38), an electrical discharge between a high-voltage electrode (36) and an earth electrode (40), these two electrodes being placed in this treatment chamber;

d) the chemical species of the plasma are carried away out of the inter-electrode region to the surface of the object or objects to be treated; and

e) the gas residues resulting from the treatment are removed from the treatment chamber.

Thus, with this atmospheric-pressure operation, it is not necessary to use complex vacuum manufacturing devices and biocidal gases.

According to the method of implementation envisaged, the moisture is introduced either directly around the object or objects to be treated (Figures 1b and 1c) or near the inter-electrode region (Figure 1a).

According to the invention, the gas mixture contains at least 10% oxygen and 10% nitrogen. It may also advantageously consist of ambient air.

Preferably, the relative humidity around the object or objects to be treated is between 50% and 100%, advantageously greater than or equal to 90%.

Depending on the method of implementation adopted, step b) of introducing the gas mixture or mixtures into the treatment chamber is carried out continuously or intermittently and the flow rate of the gas mixture or mixtures entering the treatment chamber is controlled. Likewise, step c) of creating the plasma may be preceded by a step of forced circulation of the gas

mixture or mixtures in the treatment chamber.

Step d) of carrying away chemical species of the plasma to the surface to be treated is accomplished either by using the electrical wind created by the discharge between the two electrodes or by creating a forced flow in the treatment chamber.

The invention also relates to the device for implementing this process, which comprises:

- a first gas source containing a non-biocidal gas mixture;
- at least one treatment chamber at atmospheric pressure comprising at least one sterilization region in which the object or objects to be treated are placed, this chamber furthermore including, in at least one plasma generation region separate from the sterilization region, at least two electrodes connected to a high-voltage supply in order to create a plasma, producing chemical species by generating an electrical discharge between these electrodes in the gas mixture introduced into the plasma generation region, the chemical species of the plasma being carried away out of the plasma generation region to the surface of the object or objects to be treated and the gas residues resulting from the treatment being removed to a recovery system via an outlet port of this chamber; and
- a humidifying chamber connected downstream of a second gas source in order to maintain a defined moisture content around the object or objects to be treated.

In a preferred embodiment, the first and second gas sources form a single gas source. The plasma generation region is then either connected to this single gas source via the humidifying chamber or connected directly to this single gas source, the sterilization region being connected to this single gas source via the humidifying chamber. Alternatively, the

sterilization region may also be connected to the second gas source via the humidifying chamber, the plasma generation region then being connected directly to the first gas source.

The device may include first and second relative humidity sensors placed respectively upstream of the plasma generation region and of the sterilization region. The second relative humidity sensor proves to be particularly useful when the first gas source feeds the treatment chamber directly (and therefore without passing through the humidifying chamber) and does not deliver a gas of constant moisture content.

The electrodes consist of at least one electrode with a large radius of curvature and one electrode with a small radius of curvature, one being a high-voltage electrode and the other being an earth electrode. Preferably, one or the other of the two electrodes, or both of them, are covered with a dielectric coating.

Depending on the application envisaged, the electrode with a small radius of curvature is a metal electrode which may have one of the following shapes: wire, spikes or wire having spikes, and the electrode with a large radius of curvature is a metal electrode which may have one of the following shapes: wire, plane, mesh or solid cylinder. In one embodiment particularly suitable for the sterilization of fine channels, the high-voltage electrode consists of a wire and the earth electrode consists of a mesh cylinder surrounding this wire.

Likewise, the electrodes may be mounted as an array of parallel electrodes, the high-voltage electrodes being supplied in succession or simultaneously.
Advantageously, the electrodes may be of limited usage

The high-voltage supply is provided by a low-frequency

generator delivering a DC voltage, a square wave voltage, an AC voltage or a voltage pulsed over time.

In a preferred configuration envisaged for the device, the latter comprises several treatment chambers, each treatment chamber having at least one plasma generation region connected, fixedly or not, to at least one sterilization region, the plasma generation regions being connected to a common central unit containing at least the first non-biocidal gas source (12), the humidifying chamber (14), the gas residues recovery system (22) and the high-voltage supply.

Advantageously, the sterilization region has a shape specially tailored to the object or objects to be sterilized so as to limit the production of chemical species necessary for sterilization and to optimize the rate of flow and the concentration of these sterilizing species around the object. Furthermore, the plasma generation region may be integrated into the object to be treated, of which it forms part.

In a preferred embodiment, the treatment chamber includes a case of standard shape and containing the plasma generation region, the sterilization region being formed by a removable support especially tailored to the object or objects to be treated and housed in this case.

In order to allow all the parts of an object to be treated uniformly, while reducing the propagation time on the plasma generation region to the surfaces to be sterilized, the sterilization region may include propagation regions of small cross section, making it possible to accelerate the chemical species emanating from the plasma generation region towards various parts of the object or objects to be treated.

In one particular embodiment, the sterilization region

is separate from the plasma generation region and forms an independent chamber.

One or more of the treatment or sterilization chambers may constitute reusable autonomous packaging, in the form of a transportation case, allowing the sterile post-treatment state to be maintained, or disposable packaging, in the form of a flexible bag, it being possible for the sterilization region to be divided into several separate regions after the treatment, by cutting and concomitantly sealing defined parts of this bag. Preferably, all or part of the device is placed in a Faraday cage.

Advantageously, the common central control unit includes indicating and control means associated with each sterilization chamber in order for the sterilization of the objects that it contains to be controlled individually. It also includes printing means for printing a label on which will be printed, for each sterilization chamber connected to this central control unit, an identification number specific to each chamber together with the date of the treatment and the parameters of the stabilization cycle carried out. Likewise, the treatment or sterilization chamber is provided with an electronic label which makes it possible, by means of a corresponding reader of the central control unit, to determine automatically the flow rate setpoint values and control current which are suitable for the object or objects to be treated and to calculate the time needed to sterilize these objects. This electronic label may include a flow rate sensor for measuring the flow rate of the chemical species of the plasma in the chamber together with a chemical measurement sensor.

The great flexibility of the device, relying partly on the possibility of choosing the number, the size and the position of the plasma generation regions according

to the volume and the configuration of the objects to be treated, allows it to be applied to the sterilization of a variety of objects of any shape and of any type, especially a metal, composite or heat-sensitive object, such as the sterilization of the surfaces of packages, products or production equipment, to the decontamination of the internal surfaces of air conditioning systems, or to the disinfection of containment or transfer regions. Application of the device is particularly beneficial in the medical, dental, agri-foodstuff or pharmaceutical fields.

Brief description of the drawings

Further features and advantages of the present invention will become clearer from the following description given by way of indication but implying no limitation, together with the appended drawings in which:

- Figure 1A is a diagram showing the principle of a plasma sterilization device according to the invention;
- Figures 1B and 1C are diagrams illustrating the principle of two alternative embodiments of the plasma sterilization device according to the invention;
- Figure 2 is a diagram showing the principle of a treatment chamber employed in the device of Figure 1;
- Figure 3 illustrates a first embodiment of the plasma sterilization device according to Figure 1;
- Figure 4 shows a first embodiment of a treatment chamber according to Figure 2;
- Figure 5 shows a second embodiment of a treatment chamber according to Figure 2;
- Figure 6 shows a third embodiment of a treatment chamber according to Figure 2;
- Figure 6A is an exploded view of Figure 6 illustrating particularly a configuration of electrodes;
- Figures 7A and 7B illustrate a fourth embodiment

of a treatment chamber according to Figure 2; and

- Figure 8 illustrates a second embodiment of the plasma sterilization device according to Figure 1.

Description of a preferred embodiment

The invention relates to a sterilization process which is sporicidaly effective on bacterial spores regarded by the European Pharmacopoeia as being the most resistant, namely: *Bacillus subtilis* and *Bacillus stearothermophilus*. This process makes use of a gas mixture which contains oxygen and nitrogen and in which a low-temperature plasma is created, the chemical species of which have a sterilizing effect on the object to be treated in the presence of moisture. The object to be treated is placed outside the space where the discharge occurs and the treatment is carried out at atmospheric pressure.

A plasma is gas partially activated by an electromagnetic source of sufficient energy. The species created in the plasma are ionized species (molecules or atoms), neutral species (such as radicals) or excited species. The increased reactivity of these gaseous species allows them to interact with the surfaces of the object or objects to be sterilized and thus to destroy the microorganisms present on these surfaces. For a plasma created from a simple non-biocidal gas at atmospheric pressure, the most reactive species are those having the shortest lifetime, their effectiveness depending strongly on the distance between the object and the region where the plasma is created.

A first diagram showing the principle of a plasma sterilization device for implementing the process according to the invention is illustrated in Figure 1A. This device is organized around a treatment chamber 10 divided into two regions, namely a plasma generation

region 10a, in which a plasma is created by a discharge between two electrodes, and a sterilization region 10B in which the object to be treated is placed. The discharge is generated in a non-biocidal gas mixture delivered by a gas source 12 and humidified by passing through a humidifying chamber 14. This treatment chamber may be entirely closed (and therefore sealed) or only partially open depending on the envisaged application.

The gas mixture contains oxygen and nitrogen and its composition may vary according to the nature of the object to be sterilized. The aggressivity of the mixture with respect to the constituent materials of the objects to be sterilized depends on the oxygen content of the mixture. The gas mixture must contain at least 10% oxygen and 10% nitrogen to ensure an acceptable sporacidal effect. Advantageously, this mixture may be ambient air obtained from a compressor. The relative humidity in the sterilization region, and therefore around the objects to be treated, is between 50% and 100%, advantageously greater than or equal to 90%. To improve the treatment times, the sterilization device may advantageously be temperature-controlled with a maximum temperature not exceeding 80°C in order not to damage certain types of objects, such as heat-sensitive objects.

The flow rate of the gas mixture entering the treatment chamber 10 is adjusted according to the size and to the quantity of the objects to be sterilized, by a control device 16, placed downstream of the gas source 12, allowing its flow rate and its concentration to be controlled.

The electrical discharge creates a plasma which produces species of variable lifetime. To be able to benefit from the most active species (those of short lifetime) while still operating outside the discharge

area, it is necessary to ensure that the propagation time between the plasma creation region and the object is as short as possible, and therefore that the rate of propagation between these two elements is at maximum. However, experiments conducted by the inventors have shown that, all other things being equal, the effectiveness of the proposed process decreases when the local velocity of gas around the object to be sterilized increases. It is therefore also necessary to chose a rate of flow between the plasma generation region and the sterilization region which ensures a compromise between the highest possible rate of propagation and the lowest possible local velocity.

The humidifying chamber 14 makes it possible to humidify the gas mixture to the point of saturating it with moisture under standard temperature and pressure conditions. Humidifying this mixture directly makes it possible to simplify the process by limiting the gas supplies and by simplifying the flow streams. The relative humidity of the humidified gas mixture (the carrier gas) is monitored, before the gas mixture enters the treatment chamber 10, by a suitable sensor 18a placed upstream of the plasma generation region 10a, the value of this relative humidity determining the treatment time necessary for sterilization. This is because tests carried out by the inventors have shown that the higher the relative humidity around the object, the shorter the sterilization time (see especially the earlier example).

The sterilization cycle may take place with continuous or intermittent external gas circulation or without external gas circulation. However, it is necessary for there to be gas circulation (either natural or forced) inside the chamber in order to transfer the species from the plasma generation region to the sterilization region. In the first case, the flow rate of the gas mixture is kept constant by the control device 16

throughout the sterilization cycle and the gaseous residues (effluents) resulting from the discharge are measured downstream of the treatment chamber 10 by a gas sensor 20 in order that the limiting concentrations set by the regulations (therefore in the case of ozone for example, the mean permitted exposure level in a workplace over 8 hours is 0.1 ppm according to the Occupational Safety Health Administration standard) are not exceeded before the residues are if necessary removed to a recovery system 22. In the second case, the treatment chamber is filled with the gas mixture at atmospheric pressure and then isolated before the sterilization cycle (the control device 16 having for this purpose, in particular, an isolating valve), the treatment taking place in an unreplenished gas. At the end of the sterilization cycle, the atmosphere in the treatment chamber 10 is replenished by flow of the gas mixture before the chamber is opened. In the third case, the sterilization may possibly comprise a succession of intermittent phases of gas mixture circulation and of plasma creation.

The gas sensor 20 placed downstream of the treatment chamber makes it possible using control means 24 placed, for example, near this chamber, to check the sterilization cycle in real time and to adjust the treatment time according to the gas level in the chamber and to the flow conditions. These control means are also advantageously connected to the control device 16 and to the relative humidity sensor 18a in order to control the sterilization cycle completely automatically.

It should be noted that, with the gas being humidified essentially to ensure sufficient humidity around the object to be sterilized, it is also possible, as illustrated in Figures 1B and 1C, to feed the plasma generation region with a first non-biocidal gas 12 (containing at least 10% oxygen and 10% nitrogen,

advantageously ambient air) and to feed the sterilization region with a second non-biocidal gas 26 (advantageously ambient air), but this second gas is then humidified (by passing through the humidifier 14) so as to maintain the humidity at the required level (in this case the humidity is measured upstream of the sterilization region 10b by a second humidity sensor 18b placed downstream of this humidifier). It should be noted that the first sensor 18a may remain upstream of the plasma generation region 10a, especially when the first gas is not delivered with a constant moisture content (for example, if it is ambient air). The first and second non-biocidal gases may be of the same type (Figure 1B) or of different type (Figure 1C). Of course, a flow control device 28 may also be placed downstream of the second gas source 26.

Figure 2 is a diagram showing in greater detail the principle of the treatment chamber 10 which is formed by a plasma generation region 30 and a sterilization region 32. The two regions may be separated by a metal mesh 34, it being possible for the sterilization region to have a closed or wide-open configuration in the case of surface treatment. The object 50 to be sterilized is placed on a support which must allow the sterilizing agent to circulate over its entire surface, in the sterilization region 32, that is to say outside the plasma generation region (i.e. the inter-electrode region 30 where the discharge is created).

In the example illustrated, the feed is a wet gas mixture and the plasma generation region comprises, on the one hand, an inlet port for the influx of the carrier gas and, on the other hand, two electrodes, a high-voltage electrode 36 supplied by a low-frequency high-voltage generator 38 and an earth electrode 40, these electrodes being intended to generate between them an electrical discharge called a "corona" discharge. The corona discharge is characterized by the

use of two electrodes having very different radii of curvature. The increased electric field close to the electrode with a small radius of curvature allows the voltage needed to generate the discharge to be reduced, while still using a possibly low-frequency voltage supply. One or the other of the electrodes - the one with a small radius of curvature or the one with a large radius of curvature - may be connected to the high voltage the other one being connected to earth. Of course, this electrode configuration is in no way limiting and these electrodes may also be in the form of an array of parallel electrodes, the number and the arrangement of which depends on the size and on the nature of the object to be sterilized.

The electrode 36 with a low radius of curvature (connected to the high voltage in the diagram) is made of metal, possibly covered with a dielectric, and may be in the form of spikes, a wire or a wire with spikes. When the volume of the sterilization region is large (this depending on the size and the number of objects to be sterilized), the electrodes are advantageously mounted as an array of parallel electrodes, it being possible for the high-voltage electrodes then to be supplied simultaneously or in succession during the sterilization period. The number of electrodes and their length are determined in such a way that the production of sterilizing chemical species is sufficient to obtain the concentration necessary for sterilization.

These sterilizing chemical species produced by the corona discharge in the inter-electrode space may be taken into the sterilization region either naturally by the electric wind created by the discharge between the two electrodes (the direction of the wind is from the electrode with a small radius of curvature to the electrode with a large radius of curvature) or by creating a forced flow in the treatment chamber.

The sporicidal effectiveness, and hence the sterilization time at a given point in the treatment chamber (also called reactor), depends on the rate of propagation and the local velocity. For simple flow with a constant velocity, the two values are equal: there is therefore an optimum velocity (and optimum flow rate) to ensure a minimum sterilization time.

To sterilize large chambers in a reasonable time, it is beneficial for the flow inside the chamber to cause the gas to be accelerated during its propagation phase and slowed down locally around the surface to be treated. In this way, the rate of propagation and the local velocity may be optimized independently in order to reduce the sterilization time.

The electrode 40 with a large radius of curvature (connected to earth in the diagram) is also made of metal, possibly covered with a dielectric coating, thereby preventing a passage for the electric arc during the sterilization cycle. Depending on the applications, this electrode may be in the form of a plane, in the form of a wire or in the form of a solid cylinder or else in the form of a mesh in order to facilitate the flow of the chemical species produced by the discharge. This variable geometry of the electrodes thus allows the process to be used for different applications: sterilizing packaging, sterilization of cavities and disinfection of surfaces, for example. It should be noted that since the electrodes oxidize over time, because of the discharge, the plasma generation region and/or the electrodes may be replaced after one or more treatment cycles (one cycle in the case of a one-time use).

The carrier gas inlet port 42 is preferably located close to the electrodes 36 and 40 in order to optimize its passage into the inter-electrode space, the

generation of the plasma being localized in this inter-electrode space. A gas outlet port 44 is located for its part in the sterilization region 32 downstream with respect to the natural flow direction of the gas, of the object to be treated.

In addition, in order for the system to be compatible with the electromagnetic compatibility standards, the plasma generation region in which the discharge occurs is advantageously formed by a Faraday cage 46 in order to limit any interference created by this discharge.

A current measuring device 48 capable of measuring a discharge current is connected in series with the earth electrode or with the high-voltage electrode. By measuring this current it is possible to adjust and control the voltage level necessary for generating the discharge in the inter-electrode space. By measuring the current upstream and downstream of the discharge, it is possible to check that the current injected by the source is indeed that passing to the earth electrode (differential protection).

The high-voltage generator 38 is a low-frequency generator. The voltage signal applied to the electrode 36 may be a DC voltage or a square-wave voltage, of positive or negative sign, an AC voltage or even a voltage pulsed over time.

The production of various chemical gaseous species depends on the discharge conditions. To obtain effective corona discharge conditions from the standpoint of sterilization, the voltage signal must be of the sign appropriate to the geometry of the electrodes. With a high-voltage electrode comprising one or more spikes, the voltage signal is preferably a positive DC voltage signal. With a high-voltage electrode of the wire type, it is preferably a negative DC voltage. With electrodes covered with a dielectric,

it is preferred to choose an AC voltage.

The voltage level necessary for establishing an electrical discharge in the inter-electrode space depends on the diameter of the high-voltage electrode and on the inter-electrode distance. For example, it has been found that if a 12 kV positive DC voltage is applied to a 0.125 mm diameter wire, with an inter-electrode separation of 10 mm, a corona discharge delivering a discharge current of 50 µA/cm is obtained. It should be noted that this electrical discharge may be maintained for only a fraction of the sterilization cycle.

For a given high-voltage signal type, defined by its polarity, its waveform and its frequency, the discharge conditions and the production of chemical species also depend on the intensity of the current.

The effective impedance of the discharge, giving the relationship between current and voltage, may change over time. It is preferred to control to a constant current in order to keep the same discharge conditions and the same production of chemical species so as to provide a constant sterilizing effect. In the case of linear electrodes, the discharge conditions and the production of chemical species depend on the current per unit length.

A first embodiment of a sterilization device according to the invention is illustrated in Figure 3, which shows a modular assembly with a central control unit to which various types of treatment chambers are connected. This modular assembly makes it possible to provide a large number of configurations which differ by the type of chamber used and the way in which this chamber is connected to the central control unit. It is thus possible to provide a range of chambers tailored to the requirements of each user, according to the type

of objects to be sterilized.

According to the invention, this modular assembly comprises a common central control unit containing the source of the gas mixture, the humidifying chamber and the high-voltage supply. The central control unit 60 includes one or more gas outlets (for example the outlet 62) and a corresponding number of high-voltage outputs (for example the output 64) supplying one or more treatment chambers, each having a plasma generation region 68, 70, 72 corresponding to the plasma generation region 30 and delivering sterilizing gas to a sterilizing region76, 78, 80 corresponding to the sterilization region 32 containing the objects that are to be treated. The plasma-generation and sterilization regions may form two separate regions of the same chamber (for example, the chambers 74 and 130) or they may each constitute a separate chamber constitute a separate chamber, in this case called a plasma generation chamber (in the case of the chambers 68, 70, 72) or a sterilization chamber (in the case of the chambers 76, 78, 80). Advantageously, all or part of the entire device is placed in a Faraday cage in order to limit any interference created by the discharge.

This modular configuration makes it possible to handle, simultaneously or not, a combination of chambers adapted in terms of number, shape and volume to these objects from a single central control unit having one or more high-voltage supplies and from a single gas management system (ensuring gas supply and recovery) contained in the central control unit 60. After treatment, the gas is then returned to this central control unit via one or more gas extraction inlets (for example the inlet 82).

Indicating and controlling means 84, 86, 88, 90 placed in the central control unit 60, opposite the

corresponding chambers with which they are associated, allow each chamber to be individually controlled in terms of starting the sterilization cycle and adjusting the treatment time, in terms of adjusting the appropriate flow rate setpoint and the appropriate control current and, possibly, in terms of defining the composition of the gas mixture to be used. The record of the various controls is provided by the output of a label 94 printed by a printer 96 built into the central control unit 60. For each chamber, which bears a specific identification number, it is thus possible to mention on this label the date of the treatment and the parameters of the sterilization cycle, especially its duration. The chambers may be provided with an automatic identification system, for example based on barcodes or electronic tags 98a of the RFID (Radio-frequency IDentification) type or of the IRC (InfraRed Communication) type, which by means of a corresponding reader 98b of the central control unit makes it possible to determine automatically the appropriate flow rate setpoints and the appropriate control current and to calculate the sterilization time. These electronic labels may be placed inside the chamber and be advantageously provided with sensors for controlling the sterilization cycle, especially chemical measurement sensors, for measuring, for example, the humidity, the ozone, the pH or the nitrogen dioxide content.

The sterilization region may be of variable or standardized size according to the user's requirements. By tailoring the shape and the volume of the region to the objects to be sterilized, it is possible to optimize the circulation of the sterilizing agent (its flow rate and its concentration) around the objects and thus to ensure uniform treatment.

Figures 4 to 7 illustrate various examples of chamber configurations.

In Figure 4, the sterilization chamber 76, 78 is made independently of the plasma generation chamber 68, 70. It comprises, in a case 100 which may be hermetically sealed, for example by safety clips 102 that engage with a lid 104 of this case, a support plate 106 for supporting the objects to be sterilized, for example a pair of scissors 108, a scalpel 110 and a knife 112. This support plate, which may be made of a porous material in order to facilitate the circulation of the sterilizing chemical species, divides the case into two superposed spaces, an upper space 114 and a lower space 116, within which these sterilizing species will circulate in succession. This circulation is made possible because of orifices in this plate or in the case, the configuration of the orifices being determined in order to ensure laminar flow in the sterilization region. For example, orifices 118 for passage of the chemical species may be provided in this support plate together with an inlet orifice 120 and an outlet orifice 122 for the sterilizing chemical species in the case, in the upper space 114 and the lower space 116, respectively. These inlet and outlet orifices will be fitted with non-return valves and/or advantageously provided with antibacterial filters in order to seal the internal space of the case after treatment. Sealing may also be achieved by a simple manual closure system using, for example, the clamping of a hose. Since the relationship between flow rate and velocity is a function of the degree of filling of the chamber, it is possible to measure the flow rate in the chamber after filling by means of a velocity sensor placed in the chamber so as to adjust the flow rate to the value allowing the desired flow rate to be obtained. This sensor may advantageously constitute one of the elements of the electronic label 98a.

To keep an object sterile until it is used, it should be noted that in principle it is necessary to package

the object before the treatment. The chemical species must then diffuse into the packaging and not interact with it. In the case of sterilization using heat, the steam diffuses through the packaging without interacting with it but, in the case of sterilization using gases, it is necessary in principle to develop packaging made of a specific composition which does not interact with chemical species of the plasma.

The simplicity of the modular assembly described above allows this problem to be avoided since the case naturally forms a sterilizing package which is more easily transportable and reusable. Of course, it must be kept closed after the sterilization cycle for this bacteriological protection (packaging) function. However, if it must be opened in order to use all or some of the objects that it contains; it is then necessary for a new sterilization cycle to be carried out, putting the case back into the central control unit. Furthermore, it should be noted that this case also provides a mechanical protection function (transportation or storage case).

Returning to Figure 3, this also shows two other possible configurations of the treatment chamber for sterilizing objects. In each of these configurations, the plasma (discharge) generation region and the sterilization region are placed in the same chamber, 74, 130 supplied directly with the carrier gas and with high voltage from the central control unit 60. Of course, these chambers may contain one or more plasma generation regions.

Figure 5 illustrates a first embodiment of such a chamber that can be used for general purposes. The chamber 74, which forms packaging after the treatment, comprises a case 186 of standardized shape, possibly existing in various sizes. It comprises one or more plasma generation regions 188 built directly into this

case, connectors for the gas 190, 192 and voltage 194 supplies, and an electronic label 98a. The gas connections may be sealed with respect to the outside as in the previous embodiment, but a simple bacteriological filter allowing air and moisture to pass through it may be sufficient. This filter does not need to be compatible with the sterilizing chemical species since the discharge is built into the packaging.

Housed within the case 186 is a support tray 196 chosen by the operator according to the object or objects to be sterilized. This support allows a chamber of standard shape to be converted into a chamber tailored specifically to one particular object or particular objects. This is because, as the connectors and the sealing system are entirely contained within the case, the internal support 196 may be of very simple construction, directly tailored to the volume and to the shape of the object to be treated, with a defined geometry so as to optimize the flow while ensuring maximum rate of propagation for a minimum local velocity close to the objects to be sterilized. It comprises a mesh 198 on which the object or objects are placed and propagation regions 200 of small cross section which are located in a double wall 202 of this support tray making it possible to accelerate the gas right up to the local gas supplies 204 emerging in the sterilization region 206 around the various parts of the object or objects to be treated so as to ensure sterilization over all its faces. The effluents are recovered at the end of the chamber via a passage 208 and are sent via return zones 210 contained in the double wall and via the recovery orifice 192 to the main supply region of the chamber. Propagation of the chemical species to the local supplies may also be provided by simple tubes of suitable diameter. Of course, the chamber is covered by a lid 212 kept hermetically sealed by clips 214.

It should be noted that this support tray 196 can also be used in the chamber 100, and conversely the support tray 106 of the latter chamber can be used in the chamber 74.

Figures 6 and 6A illustrate a second embodiment of a treatment chamber more especially suitable for sterilizing an endoscope and provided with three independent plasma generation regions.

This treatment chamber 130 is characterized by a particular geometry of the electrodes constituting the plasma generation region which also makes it possible to produce *in situ* sterilizing chemical species. This is because, with conventional sterilization techniques, the internal areas of the objects may be difficult to sterilize if the active principles cannot reach them easily. This is particularly a problem in the case of cavities or the inside of tubes, such as, for example, in the case of the channels of endoscopes. However, the sterilization process of the invention, which can be applied perfectly well to the sterilization of these cavities, also allows this problem of access to these internal areas to be solved simply.

The chamber 130 is in the form of a case that can be hermetically sealed and the internal space of which (the actual sterilization region) is arranged according to the shape of the object to be treated. Thus, in the example illustrated, with the endoscope folded flat in the chamber, three separate plasma generation regions are defined, one region 132 at its head 134 and the other two regions 136, 138 distributed uniformly over the external surface of its channel 140. The carrier gas is brought into the case in the central control unit 60 via at least one external connection 142 and is redistributed to the plasma generation regions via internal channels 144, 146, 148 respectively. The

electrodes of these plasma generation regions are connected in particular via links 150, 152 to a first external high-voltage connector 154 linked with a first corresponding compatible connector 158a of the common central control unit 60. After treatment, a link 160 allows the gas to be returned to this central control unit 60. To sterilize the internal surface of the channel of the endoscope a system of specific wire electrodes (see Figure 6A) is furthermore provided. The high-voltage electrode 162, supplied via a second connector 156 also connected to a connector 158b of the central control unit, may be in the form of a wire possibly having spikes and placed along the longitudinal axis of this channel, and the earth electrode 164 advantageously consists of a mesh cylinder placed around this high-voltage electrode. It is also conceivable to have a configuration with two wire electrodes organized as a bundle. In all cases, for reasons of discharge stability, these wire electrodes must be coated with an insulator, as is the case for an enamelled wire for example. This electrode system is placed in the channel of the endoscope before the start of the sterilization cycle. However, in certain cases it may be preferable to incorporate the discharge electrodes (which will possibly be replaceable) directly into the object to be treated. This is because it is quite conceivable for the plasma generation region to be incorporated into the object to be treated right from its design stage, the said region then forming part of the object. The gaseous effluents of the sterilization region 166 may be removed from the connector 159, again via the link 160. As in the previous example, non-return values and/or anti-bacterial filters are provided at the interfaces with the case 130 in order to seal it after it has been disconnected from the common central control unit 60. Individual control of this case is provided by an indicating and control means 92 placed in the central control unit.

The embodiments of the chamber proposed previously use the sterilization chamber as packaging for the object or objects to be treated. Since it is necessary to open the chamber completely in order to use an object, all the objects present, even those not used, will have to be resterilized before next being used.

Figures 7A and 7B provide yet another configuration of the treatment chamber addressing the problem of having to have objects sterilized simultaneously but used separately. In this third embodiment, all or part of the treatment chamber is produced in a flexible material allowing individual sealing after the treatment this sealing allows the objects contained in the chamber to be separated after sterilization without any risk of contamination and consequently allows the various objects to be used separately.

In a preferred embodiment, the chamber is a bag 220 having at least one transparent face and having an opening in order to be able to introduce the various objects. The material of the bag is chosen so as to allow a cutting operation and a concomitant sealing operation, for example heat sealing or any other equivalent process. The size and shape of the bag are determined by the operator according to his requirements. This bag contains a plasma source 22 at one end and an extraction fitting 224 at the other. Both the plasma source and the extraction fitting may be sealed to the bag by the operator or may be incorporated into the bag directly at its design stage. After the objects 226, 228, 230 to be treated have been put into the bag, it is sealed at its ends so as to seal it from the outside while allowing the gas to flow from one end of the chamber to the other. This flow may be facilitated either by slightly pressurizing the bag, so as to inflate it, or by using the shape of the plasma source and of the connection fitting to separate

it. The plasma source and the extraction fitting are connected to the central control unit 60 via links 142, 160 respectively. An electrical link 158 supplies the plasma source with high voltage.

After the sterilization cycle, a sealing machine 232 is used to isolate the objects from one another in individual sterile sachets 234, 236, 238 and from the source and the extraction fitting (see Figure 7B). This operation entails no risk of contamination from the outside. Isolating the objects allows these various objects to be used separately. After the treatment, the plasma source and the extraction fitting may be thrown away or recycled. This principle can also be used in the case of the rigid chambers by placing various chambers inside a bag, the bag acting as a cover at the end of sterilization.

Finally, we point out that, in a basic configuration (not shown), all the elements needed for sterilization (source of carrier gas, humidifier, electrodes, high-voltage supply) together with a treatment chamber, which may contain one or more objects to be treated simultaneously, may, of course, be placed in a single closed module or chamber.

A second embodiment of a plasma sterilization device is illustrated in Figure 8. This relates more particularly to the disinfection of surfaces. This is because the process of the invention allows the design of a device for disinfecting surfaces in the ambient air, which can be used for example for disinfecting floors. The times required for disinfection are much shorter than those required for sterilization, and therefore allow the development of a system for treating surfaces by moving the plasma generation region thereover. In this case, the treatment provides thorough disinfection against all microorganisms (bacteria, yeast, fungi and mites) and it may be incorporated into a cleaning device since

the objects to be sterilized do not need to be dried before the sterilization treatment.

In such a surface disinfection device, the sterilization region does not consist of a closed chamber but the open area lying immediately downstream of the plasma generation region. This device is in fact in the form of a brush 168 with a handle 170 fastened to a brush body 172 forming a protective enclosure for the various elements needed to generate a plasma, especially the electrode system with its high-voltage electrode 174 and its earth electrode, possibly consisting of a simple metal mesh 176. The electrodes have the same characteristics as those described in the first embodiment, the high-voltage electrode possibly being made, for example, in the form of spikes, a wire or a wire with spikes. However, for reasons of effectiveness, there are in this case two high-voltage electrodes 174 which thus form a two-plate structure, possibly having spikes, the gas mixture entering the middle of this structure. With this specific structure, the electrode system thus creates two plasma curtains in the inter-electrode space. Of course, this electrode system can be repeated several times in parallel in larger devices. The electrodes are advantageously supplied by one or more batteries 178 incorporated into the body of the brush 172.

In this embodiment, the gas mixture consists simply of ambient air introduced into the brush body via an external air intake 180 and then humidified in a water refill unit 182. An air compressor possibly provided with a filtration device may optionally be placed just behind the air intake before the water refill unit.

The operating principle of this brush 168 is similar to that governing the previous chambers. The gas mixture consisting of humidified air is converted into a plasma between the electrodes and the chemical species

produced by the corona discharge in the inter-electrode space are conveyed, on the one hand, by the electrical wind, the direction of which is from the electrode with a small radius of curvature (the two high-voltage electrode plates) to the electrode with a large radius of curvature (the mesh of the earth electrode) to the surface to be disinfected, located downstream of the earth electrode, and, on the other hand, by forced circulation. This then results in disinfection of the surface, the gas being extracted naturally through the mesh 176. This disinfection device may include a system of rollers (not shown) in order to travel over all of the surface in question.

It should be noted that the circulation of the carrier gas must be distributed uniformly in the electrode system, and especially between the two high-voltage electrodes, in order to favour the replenishment of air and to force the carrier gas to pass through the two plasma curtains.

The following example will show more clearly the effectiveness of the plasma sterilization process according to the invention, the sterilizing effect of which is compared according to the composition of the carrier gas and according to the type of bacterial spores.

Tests were carried out with biological indicators containing microorganisms particularly resistant to sterilization by gases. These were *Bacillus subtilis* (coming from the Collection de l'Institut Pasteur [*Pasteur Institute Collection*], CIP 77.18) and spores of *Bacillus stearothermophilus* (coming from the Collection de l'Institut Pasteur, CIP 52.81) which were inoculated on glass slides. Each specimen contained 10^6 spores of the bacillus.

Each biological indicator was placed in the

sterilization region and exposed to a treatment cycle. During the treatment, the flow rate of the gas mixture was 0.2 litre/min in a 0.5 litre treatment region at atmospheric pressure and at ambient temperature. The high-voltage electrode was a steel plate 5 cm in length having spikes over its entire length. The earth electrode was a steel disc 5 cm in diameter. The inter-electrode distance was 10 mm. The corona discharge was obtained by applying a positive DC voltage of 11 kV to the high-voltage electrode.

After the biological indicators had been exposed to a treatment cycle of 20 minutes, they were sterilely transferred to a nutritive medium. The biological indicators containing *Bacillus subtilis* spores were incubated at 37°C for 15 hours. The biological indicators containing *Bacillus stearothermophilus* spores were incubated at 56°C for 30 hours.

Composition of the carrier gas	Relative humidity	% of *Bacillus subtilis* spores remaining after 20 minutes of treatment	% of *Bacillus stearothermophilus* spores remaining after 20 minutes of treatment
20% O_2 in nitrogen	100%	*	0.01
	0%	100	100
20% O_2 in argon	100%	0.05	50
	0%	100	100

*less than 1 spore remaining

It is clear that the process according to the invention is particularly effective when the carrier gas contains a high relative humidity. In contrast, with a conventional process using a rare gas, such as argon, the effect on *Bacillus subtilis* spores is relatively weak, and on *Bacillus stearothermophilus* spores even very weak, thereby not allowing a quality level sufficient for sterilization to be achieved.

Thus, the invention relates to a remote plasma sterilization process at room temperature and at atmospheric pressure (or a pressure close to atmospheric pressure), by means of a corona discharge established in a non-biocidal gas mixture containing oxygen and nitrogen, and in the presence of moisture. This process has a sporicidal effect on both *Bacillus subtilis* and *Bacillus stearothermophilus* spores in less than one hour. This process furthermore makes it possible to sterilize objects and surfaces regardless of their shape and their nature, be they metallic, composite or heat-sensitive.

Corona-discharge plasma sterilization appears to be an innovative technique that can be used at room temperature in a gas at atmospheric pressure without toxic residues. The process thus describe is both simple in design, since the chamber does not need to withstand large pressure differences, the high-voltage supply system is a low-frequency supply and the gas supply system is simplified, and simple to use, since there are no chemicals to be handled before and after the sterilization cycle and the risks of pollution are limited. Furthermore, it has a low manufacturing cost because of the use of simple gas atmospheres and simple electrode structures.

The proposed applications essentially relate to the medical field, but the process may, of course, extend to other industrial applications, for example in the agri-foodstuff and pharmaceutical fields. The great flexibility of the device furthermore allows sterilization of surfaces of packaging, of products or of production equipment, and the disinfection of containment or transfer areas. The device can also be used to decontaminate the internal surfaces of air conditioning systems.

CLAIMS

1. Process for the plasma sterilization of at least one object, in which:
a) the object or objects (50) to be treated are placed in a treatment chamber (10) at substantially atmospheric pressure;
b) one or more non-biocidal gas mixtures, at least one of which contains moisture, are introduced into this treatment chamber;
c) a plasma, producing chemical species from one of the gas mixtures, is created by generating, by means of a high-voltage supply (38), an electrical discharge between a high-voltage electrode (36) and an earth electrode (40), these two electrodes being placed in this treatment chamber;
d) the chemical species of the plasma are carried away out of the inter-electrode region (30) to the surface of the object or objects (50) to be treated; and
e) the gas residues resulting from the treatment are removed from the treatment chamber.

2. Process according to Claim 1, characterized in that the moisture is introduced directly around the object or objects (50) to be treated.

3. Process according to Claim 1, characterized in that the moisture is introduced near the inter-electrode region (30).

4. Process according to any one of Claims 1 to 3, characterized in that the gas mixture contains at least 10% oxygen and 10% nitrogen.

5. Process according to Claim 4, characterized in that the gas mixture consists of ambient air.

6. Process according to any one of Claims 1 to 5, characterized in that the relative humidity around

the object or objects (50) to be treated is between 50% and 100%.

7. Process according to Claim 6, characterized in that the relative humidity around the object or objects (50) to be treated is greater than or equal to 90%.

8. Process according to Claim 1, characterized in that step b) of introducing the gas mixture or mixtures into the treatment chamber (10) is carried out continuously or intermittently.

9. Process according to Claim 8, characterized in that the flow rate of the gas mixture or mixtures entering the treatment chamber (10) is controlled.

10. Process according to Claim 1, characterized in that step c) of creating the plasma is preceded by a step of forced circulation of the gas mixture or mixtures in the treatment chamber (10).

11. Process according to Claim 1, characterized in that step d) of carrying away the chemical species of the plasma to the surface (50) to be treated is accomplished by using the electrical wind created by the discharge between the two electrodes (36, 40).

12. Process according to Claim 1, characterized in that step d) of carrying away the chemical species of the plasma to the surface (50) to be treated is accomplished by creating a forced flow in the treatment chamber (10).

13. Device for the plasma sterilization of at least one object, characterized in that it comprises:

- a first gas source (12) containing a non-

biocidal gas mixture;

- at least one treatment chamber (10) at atmospheric pressure comprising at least one sterilization region (10b, 32) in which the object or objects (50) to be treated are placed, this chamber furthermore including, in at least one plasma generation region (10a, 30) separate from the sterilization region, at least two electrodes (36, 40) connected to a high-voltage supply (38) in order to create a plasma, producing chemical species by generating an electrical discharge between these electrodes in the gas mixture introduced into the plasma generation region, the chemical species of the plasma being carried away out of the plasma generation region to the surface of the object or objects to be treated and the gas residues resulting from the treatment being removed to a recovery system (22) via an outlet port (44) of this chamber; and

- a humidifying chamber (14) connected downstream of a second gas source (12, 26) in order to maintain a defined moisture content around the object or objects (50) to be treated.

14. Device according to Claim 13, characterized in that the first and second gas sources form a single gas source (12).

15. Device according to Claim 14, characterized in that the plasma generation region (10a, 30) is connected to this single gas source via the humidifying chamber (14).

16. Device according to Claim 14, characterized in that the plasma generation region (10a, 30) is connected directly to this single gas source (12), the sterilization region (10b, 32) being connected to this single gas source via the humidifying chamber (14).

17. Device according to Claim 13, characterized in that the sterilization region (10b, 32) is connected to the second gas source (26) via the humidifying chamber (14), the plasma generation region (10a, 30) being connected directly to the first gas source (12).

18. Device according to Claim 16 or Claim 17, characterized in that it includes a second relative humidity sensor (18b) placed upstream of the sterilization region (10b, 32).

19. Device according to any one of Claims 15 to 17, characterized in that it includes a first relative humidity sensor (18a) placed upstream of the plasma generation region (10a, 30).

20. Device according to any one of Claims 13 to 19, characterized in that the gas mixture contains at least 10% oxygen and 10% nitrogen.

21. Device according to Claim 20, characterized in that the gas mixture consist of ambient air.

22. Device according to Claim 21, characterized in that the ambient air is compressed before it is humidified.

23. Device according to any one of Claims 13 to 22, characterized in that the sterilization region (10b, 32) has a relative humidity of between 50% and 100%, advantageously greater than or equal to 90%.

24. Device according to any one of Claims 13 to 23, characterized in that it comprises at least one electrode with a large radius of curvature and one electrode with a small radius of curvature, one

being a high-voltage electrode (36) and the other being an earth electrode (40).

25. Device according to Claim 24, characterized in that the electrode with a small radius of curvature is a metal electrode which may have one of the following shapes: a wire, spikes or a wire having spikes.

26. Device according to Claim 24, characterized in that the electrode with a large radius of curvature is a metal electrode which may have one of the following shapes: a wire, a plane, or a mesh or solid cylinder.

27. Device according to Claim 25 or Claim 26, characterized in that one or the other of the two electrodes, or both electrodes, are covered with a dielectric coating.

28. Device according to Claim 25 and Claim 26, characterized in that the high-voltage electrode consists of a wire (162) and in that the earth electrode consists of a mesh cylinder (164) surrounding this wire.

29. Device according to Claim 24, characterized in that the electrodes are mounted as an array of parallel electrodes, the high-voltage electrodes being supplied in succession or simultaneously.

30. Device according to any one Claims 13 to 29, characterized in that the electrodes are of limited usage.

31. Device according to any one Claims 13 to 30, characterized in that the high-voltage supply (38) is provided by a low-frequency generator delivering a DC voltage, square-wave voltage or AC

voltage, or a voltage pulsed over time.

32. Device according to Claim 13, characterized in that it comprises several treatment chambers, each treatment chamber having at least one plasma generation region (68; 70; 72; 132, 136, 138; 188) connected, fixedly or not, to at least one sterilization region (76; 78; 80; 166; 206), the plasma generation regions being connected to a common central unit (60) containing at least the first non-biocidal gas source (12), the humidifying chamber (14), the gas residues recovery system (22) and the high-voltage supply (38).

33. Device according to Claim 32, characterized in that the sterilization region (166; 206) of the treatment chamber (74, 130) has a shape specially tailored to the object or objects (134, 140; 226, 228, 230) to be sterilized so as to limit the production of chemical species necessary for sterilization and to optimize the rate of flow and the concentration of these sterilizing species around the object.

34. Device according to Claim 33, characterized in that the treatment chamber (74) includes a case (186) of standard shape and containing the plasma generation region (188), the sterilization region being formed by a removable support (196) especially tailored to the object or objects to be treated and housed in this case.

35. Device according to Claim 32 or Claim 34, characterized in that the sterilization region includes propagation regions (200) of small cross section making it possible to accelerate the chemical species emanating from the plasma generation region (188) towards various parts of

the object or objects to be treated.

36. Device according to Claim 32, characterized in that the plasma generation region is incorporated into the object to be treated and forms a part thereof.

37. Device according to Claim 32, characterized in that the sterilization region is separate from the plasma generation region and forms an independent chamber (76, 78, 80).

38. Device according to Claim 32 or Claim 37, characterized in that one or more of the treatment or sterilization chambers constitute reusable autonomous packaging, in the form of a transportation case, allowing the sterile post-treatment state to be maintained.

39. Device according to Claim 32 or Claim 37, characterized in that one or more of the treatment or sterilization chambers constitute disposable packaging, in the form of a flexible bag (220), it being possible for the sterilization region to be divided into several separate regions (234, 236, 238) after the treatment, by cutting and concomitantly sealing defined parts of this bag.

40. Device according to any one of Claims 32 to 39, characterized in that all or part of the device is placed in a Faraday cage.

41. Device according to Claim 32, characterized in that the common central control unit (60) includes indicating and control means (84, 86, 88, 90) which are associated with each sterilization chamber in order for the sterilization of the objects that it contains to be controlled individually.

42. Device according to Claim 41, characterized in that the common central control unit (60) includes printing means (96) for printing a label (94) on which will be printed, for each sterilization chamber connected to this central control unit, an identification number specific to each chamber together with the date of the treatment and the parameters of the stabilization cycle carried out.

43. Device according to Claim 32, characterized in that the treatment or sterilization chamber is provided with an electronic label (98a) which makes it possible, by means of a corresponding reader (98b) of the central control unit (60), to determine automatically the flow rate setpoint values and control current which are suitable for the object or objects to be treated and to calculate the time needed to sterilize these objects.

44. Device according to Claim 43, characterized in that the electronic label includes a velocity sensor for measuring the flow rate of the chemical species of the plasma in the chamber.

45. Device according to Claim 43, characterized in that the electronic label includes a chemical measurement sensor.

46. Application of the device of Claims 13 to 45 to the sterilization of objects of any shape and of any nature, especially be they metallic, composite or heat-sensitive.

47. Application of the device of Claims 13 to 45 to the sterilization of the surfaces of packaging, of products or of production equipment.

48. Application of the device of Claims 13 to 45 to the decontamination of the internal surfaces of air conditioning systems.

49. Application of the device of Claims 13 to 45 to the disinfection of containment or transfer areas.

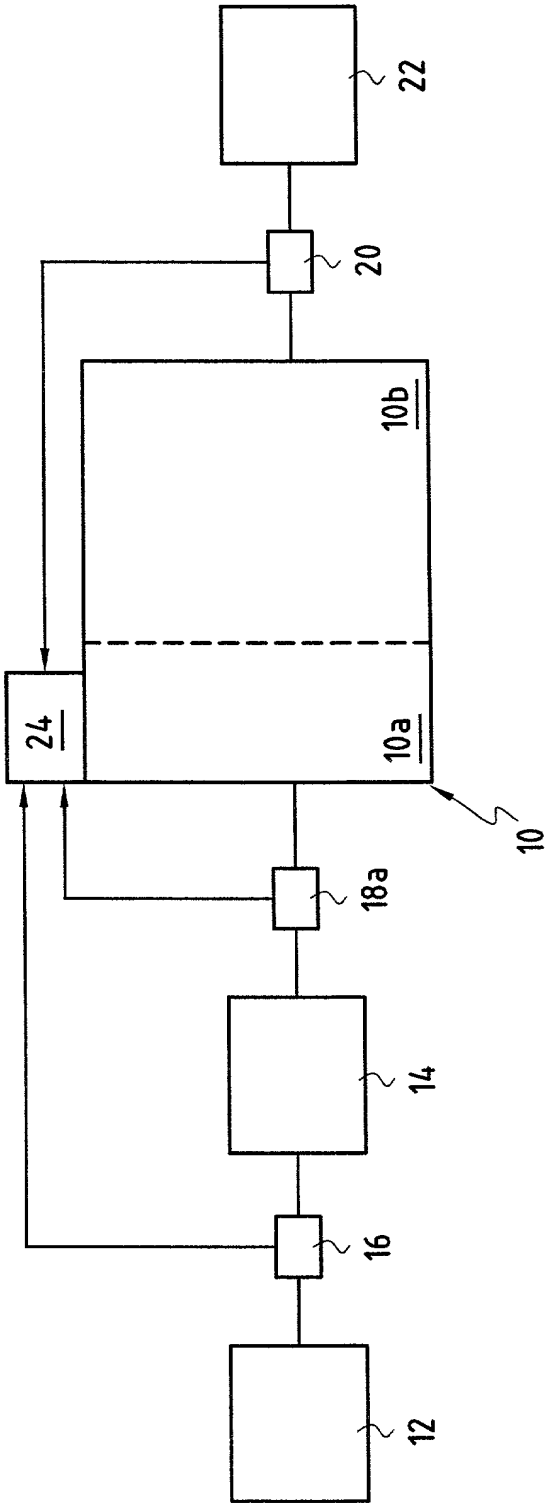

FIG.1A

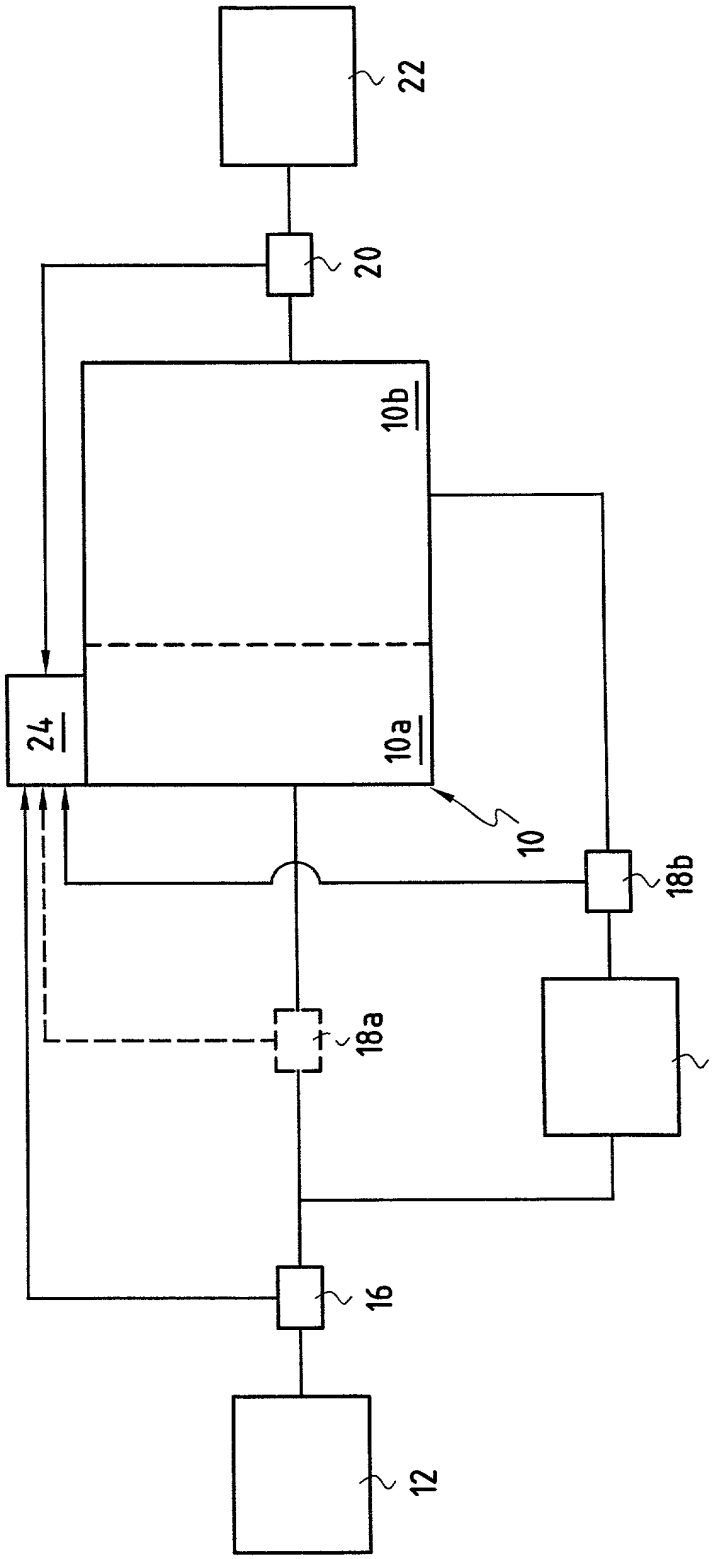

FIG.1B

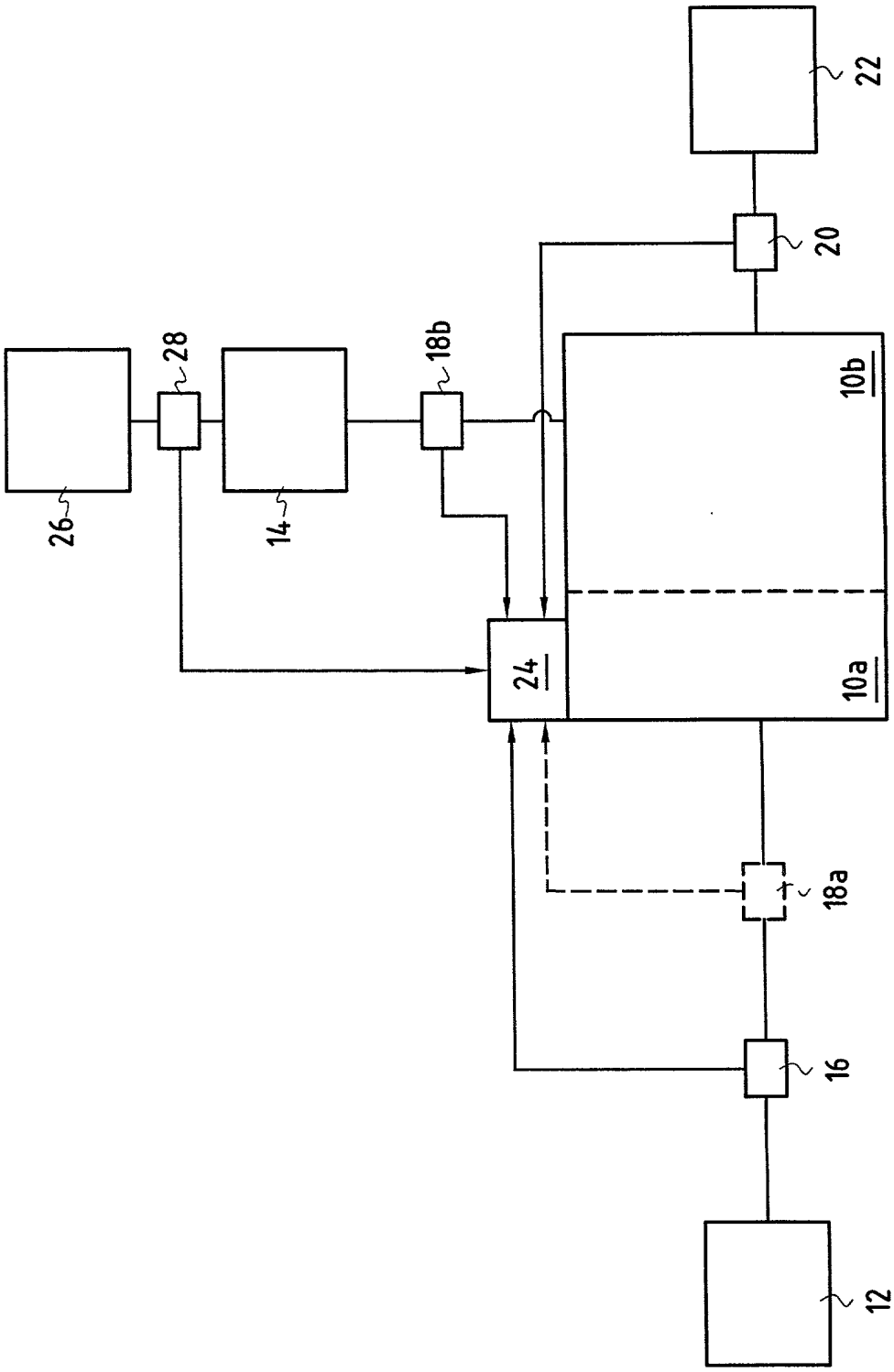

FIG.1C

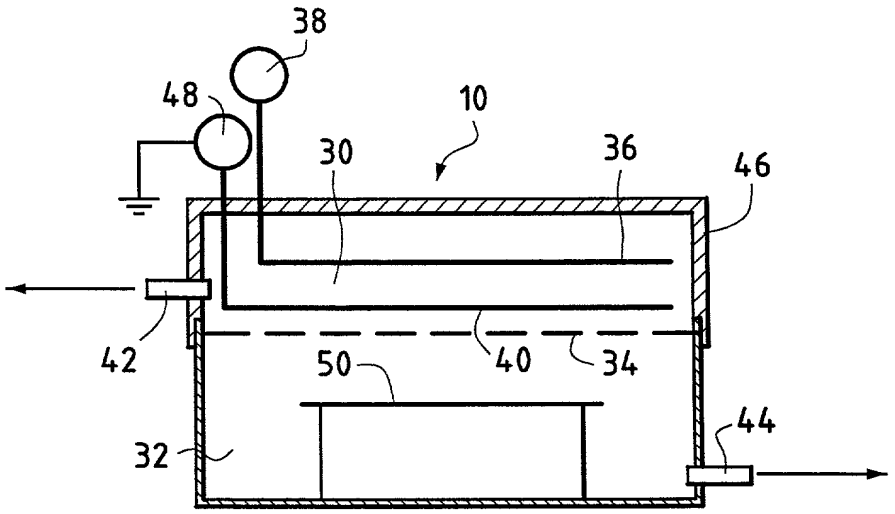
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FIG.2

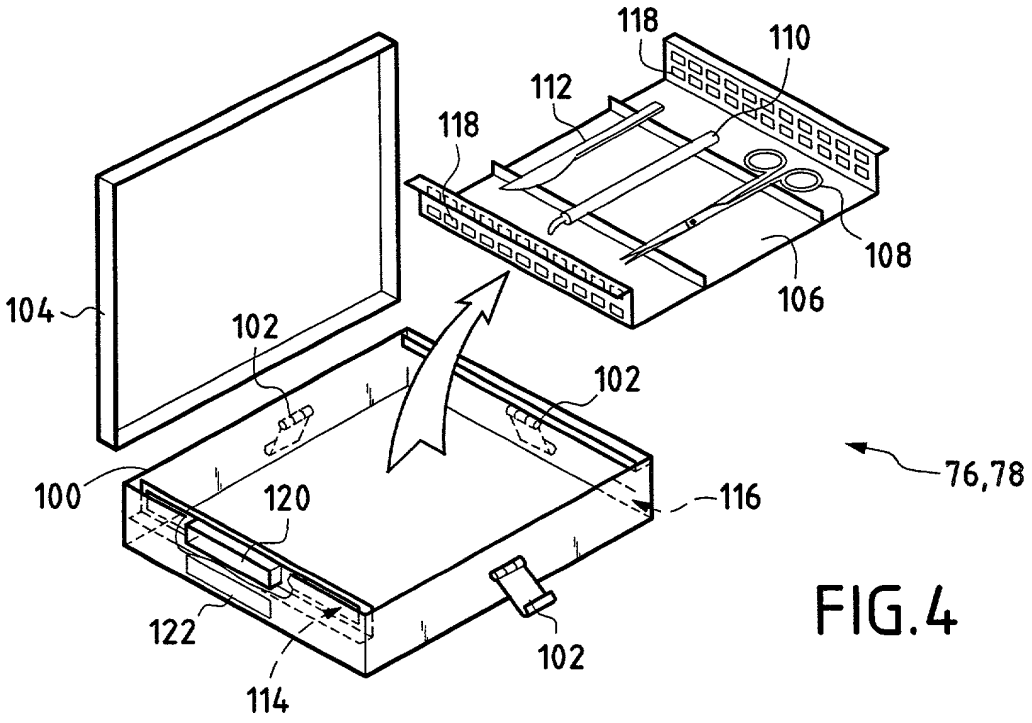
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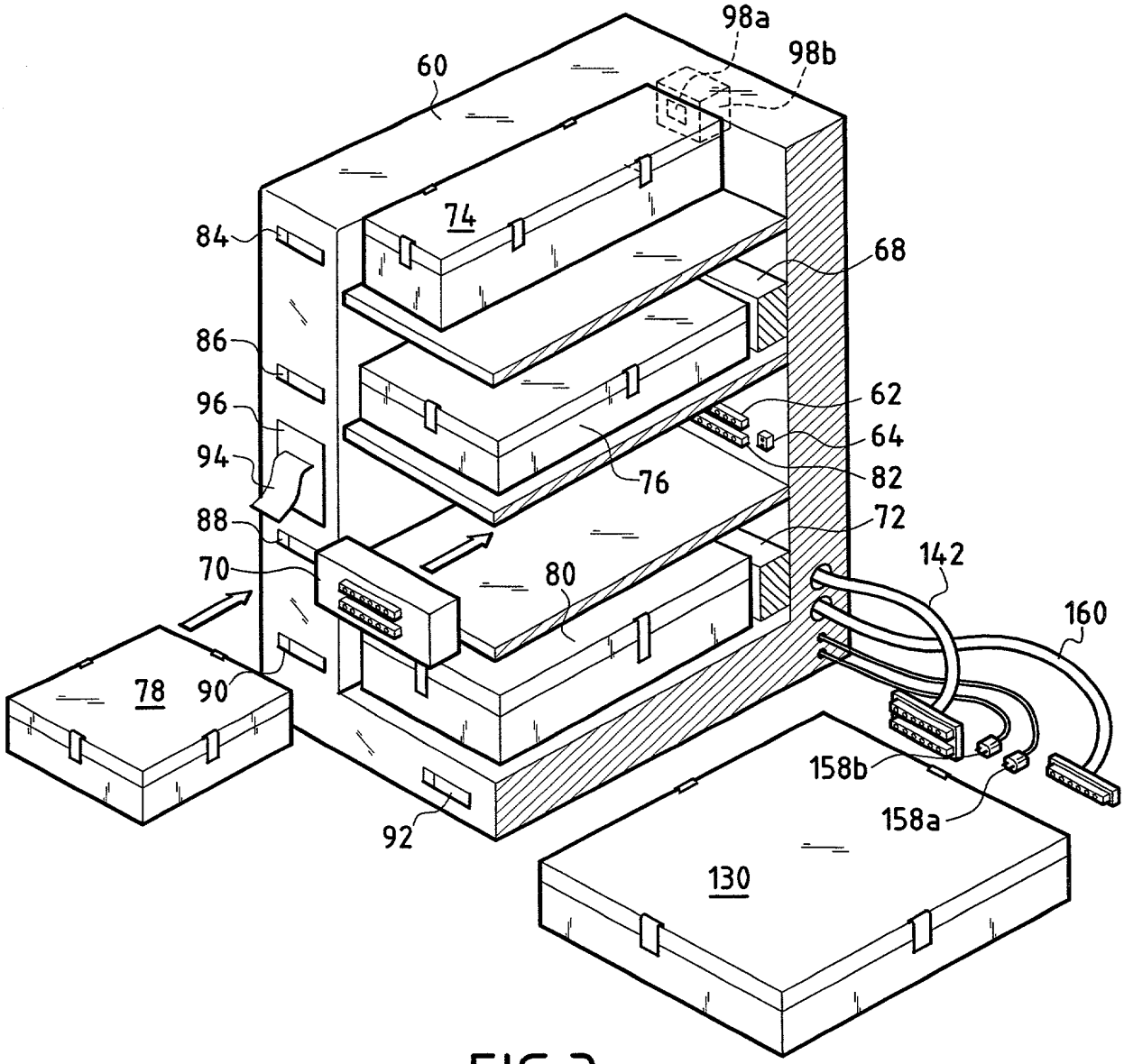
FIG.4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158a
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FIG.3

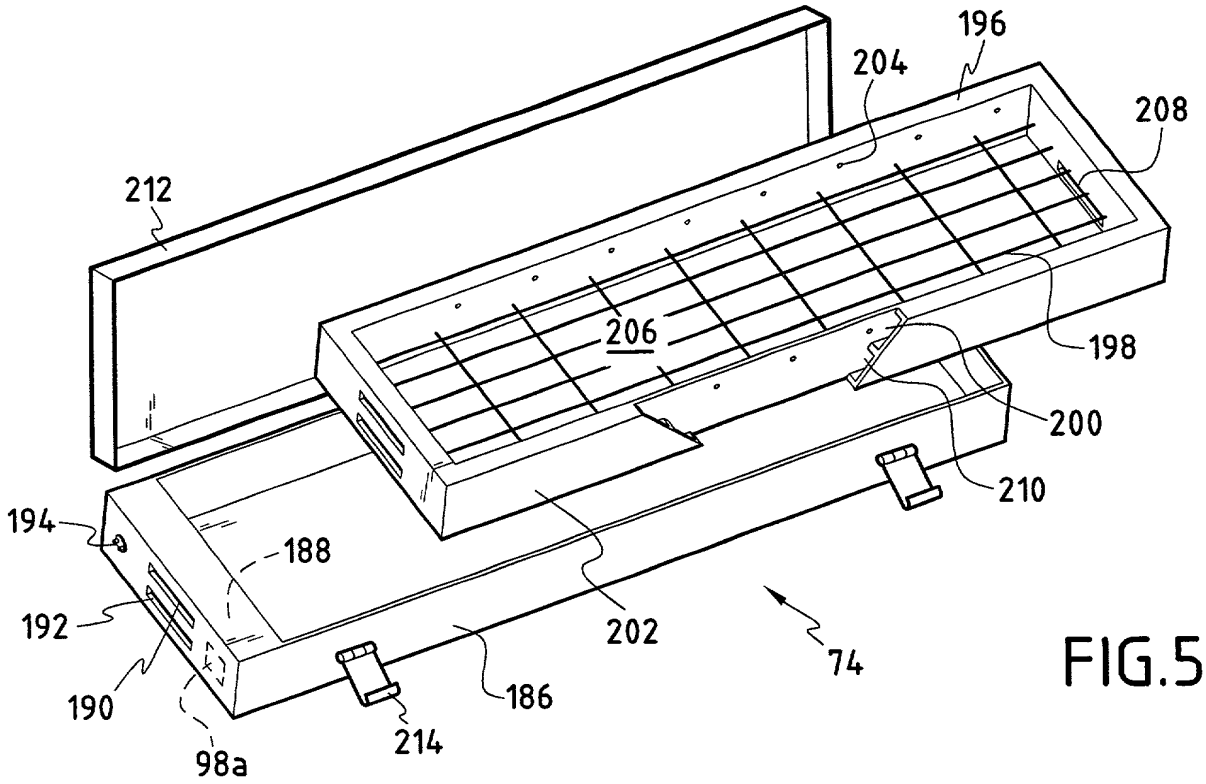

FIG.5

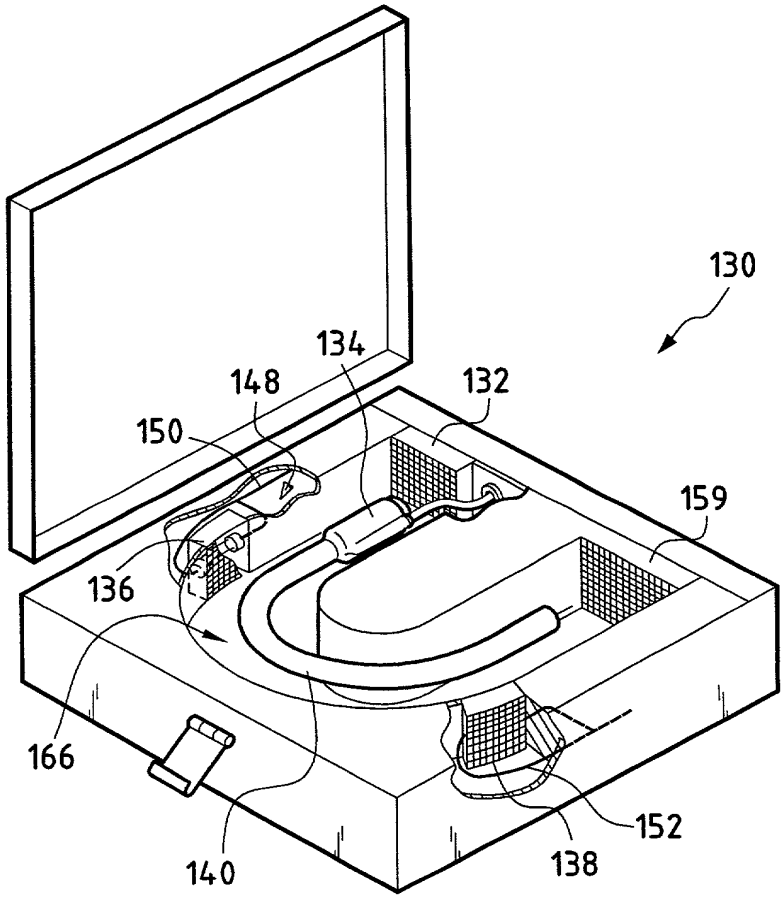

FIG.6

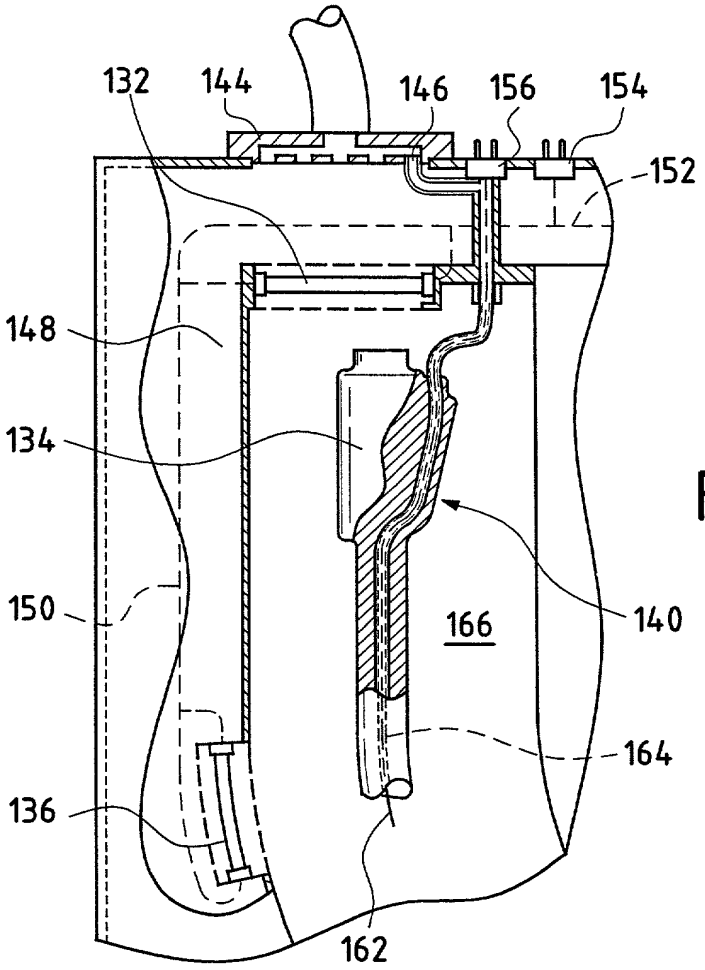
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FIG.6A

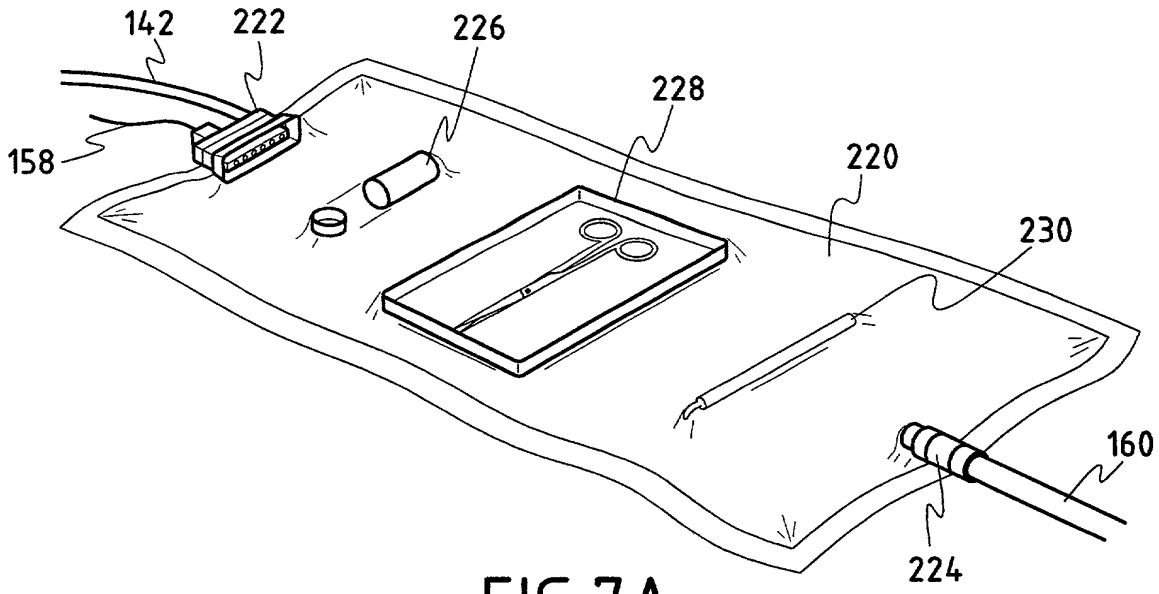
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FIG.7A

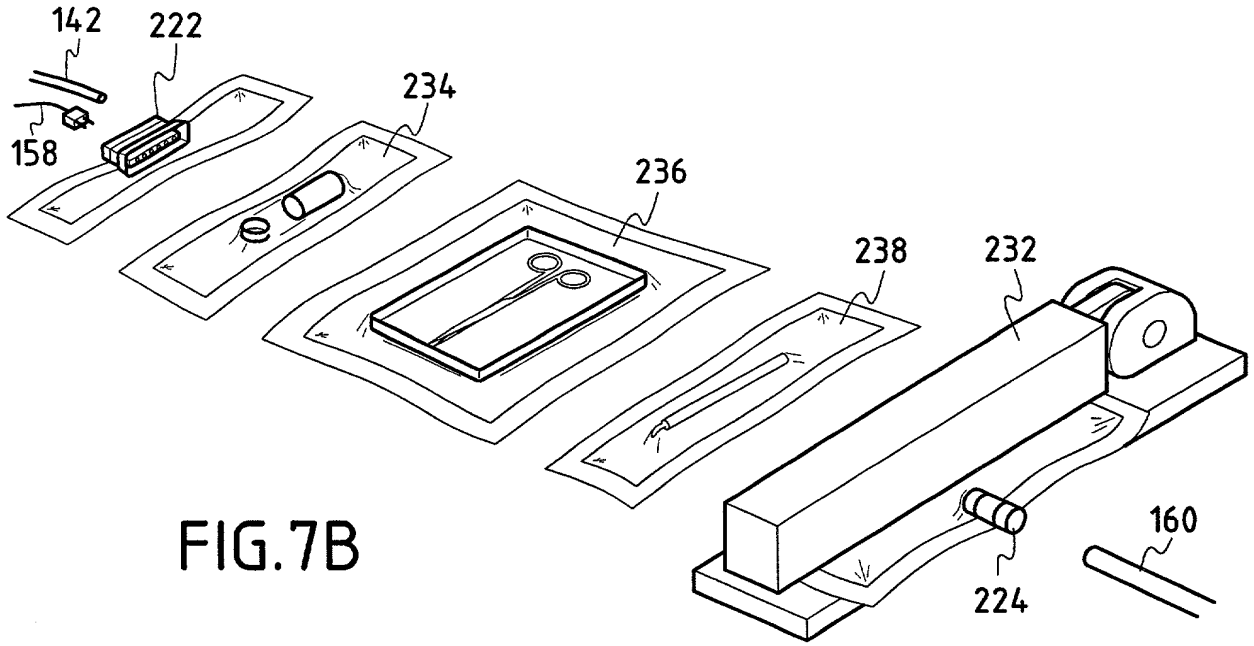

FIG.7B

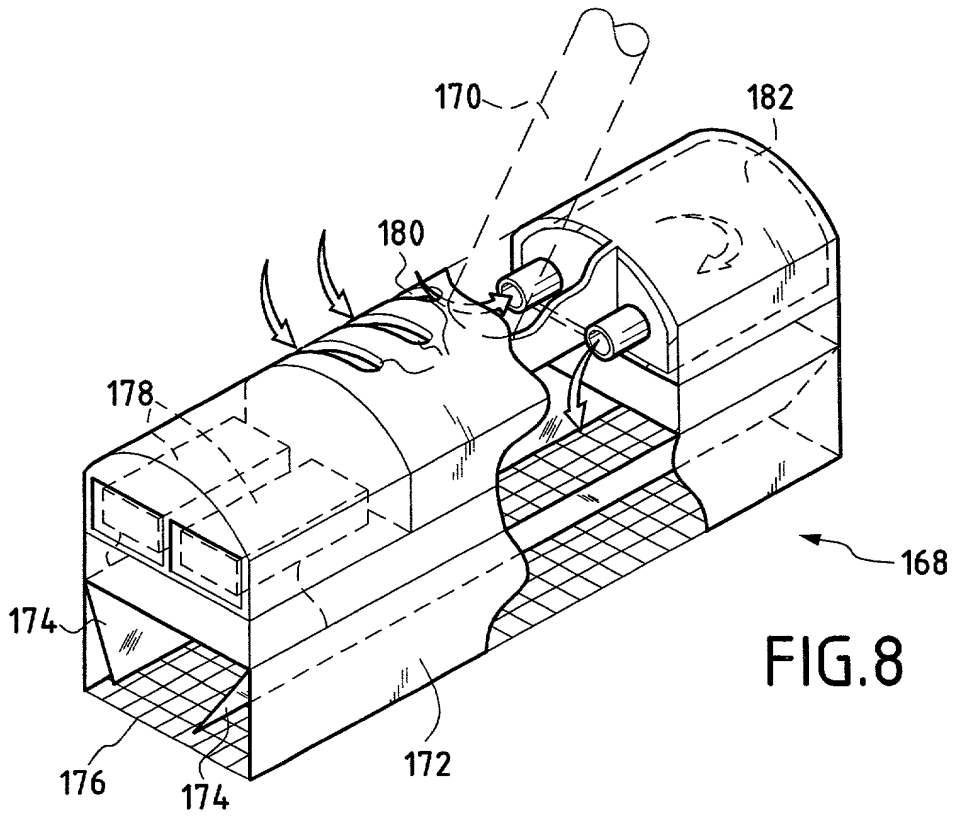

FIG.8

)1/2000 FORM 11

Attorney
Docket No.:

DECLARATION AND POWER OF ATTORNEY

As a below-named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name;

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

Method and devices for sterilization by plasma

the specification of which (check one):

[ ] is attached hereto. [ ] was filed _____ as Application No._____
amended on _____(if applicable).

[X] was filed as PCT International Application No. PCT/FR00/00644 on
and was amended under PCT Article 19 on March 16, 2000 (if applicable).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the patentability of this application in accordance with Title 37, Code of Federal Regulations §1.56(a).

I hereby claim foreign priority benefits under Title 35, USC §119(a)-(d) of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s)		Date Filed	Priority Claimed	
99/03200	France	16/03/1999	[X] Yes	[ ] No
(Number)	(Country)	(Day/Month/Year)		
			[ ] Yes	[ ] No
(Number)	(Country)	(Day/Month/Year)		

I hereby claim the benefit under Title 35, USC §119(e) of any United States provisional application(s) listed below:

(Application Number)	(Filing Date)
(Application Number)	(Filing Date)
(Application Number)	(Filing Date)
(Application Number)	(Filing Date)

Express Mail Number
EL 751779258 US

Attorney
Docket No.:

I hereby claim the benefit under Title 35 USC §120 of any United States application(s) listed below and insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35 USC §112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §1.56(a) which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

(Application No.)	(Filing Date)	(Patented/pending/abandoned)
(Application No.)	(Filing Date)	(Patented/pending/abandoned)
(Application No.)	(Filing Date)	(Patented/pending/abandoned)

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) to prosecute this application and transact all business connected therewith in the Patent and Trademark Office, and to file with the USRO any International Application based thereon.

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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Attorney
Docket No.:

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